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Plastics

Dealing with the Manufacture, Uses and Potentialities of Plastic Materials

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NOTICES

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SAVE PAPER

More than ever is paper waste required for our war industries. Waste paper makes munitions in a hundred forms—from shell cases to aeroplane parts.

The fact that goods made of raw materials in short supply because of war conditions are advertised in this journal should not be taken as an indication that they are necessarily available for export.

EDITORIALS

The Science of Big Molecules

MOST of us have regarded the plastics industry merely as a cross section of the chemical and engineering industries and have left it at that. But we think it is important to clarify its actual situation in the scientific and technical world by putting a narrower significance to it. The plastics industry is an industry which produces big molecules—gigantic ones—and which manipulates them to serve mankind.

These adjectives are not used here merely to impress the reader but rather to indicate why they are produced and perhaps the road of future development.

The inorganic matter of the world, that is the metals, minerals and compounds made from them, are all composed of comparatively small molecules. The weight of these molecules, even of the compounds of heavy metals, is low compared with the molecules of the plastic industry; they very rarely exceed 1,000 times the weight of the hydrogen atom which is taken as a standard. The molecule of common salt is only 58 times the weight of the hydrogen atom. Moreover, it is difficult and generally impossible to add new atoms to an inorganic compound.

The World of Organic Molecules

The organic or carbon containing molecules in the universe are very different. While many are small and of low weight, many others exist that are large in size and heavy in weight. Thus the naturally occurring cellulose in cotton and other fibres is a very large molecule tens of thousands times the weight of the hydrogen atom. So are the molecules of glue, casein, starch, sugar, rubber. These are so complicated that we do not know their exact molecular weight.

Furthermore, with many low molecular weight organic compounds we can keep on combining them together or adding others in order to get molecules of high weight. Organic compounds can be made by man with molecular weights of 5,000, 20,000 and even 1,000,000.

The importance to our industry is not that these molecular weights are high, but that such molecules possess special characteristics. First, all these very big molecules are solids or at least fibrous, and since the plastic industry is one that deals with structural substances we must have solids for our raw material, e.g., cotton, casein, rubber, etc., or make them solid from the liquid or gaseous raw materials of the world, e.g., acetylene, benzene, alcohol, petroleum, carbolic acid, formaldehyde, etc. Thus although most liquid organic compounds are dielectrics, that is, they do not allow the passage of electricity, they are useless as structural materials because they are not solid. Hence the value of plastics to the electrical industry.

Secondly, these large molecules are packed together in very special, although not clearly defined, ways, sometimes in linear bunches, sometimes in spiral bunches, sometimes in bunches that are both long and thick. The result is that on the whole the method and the denseness of the packing give the properties of strength or resilience or insolubility, or resistance to water. This is well known in the case of the natural fibres—silk and flax are as strong as steel—and in the case of rubber.

The man-made big molecules are also strong, resilient or insoluble and the time is rapidly approaching when he will be able to forecast with fair accuracy the properties of a new big molecule before it has been made.

Finally, we must mention the most important property of the big molecules we handle. They are tightly packed, but not so tightly as to prevent them loosening under comparatively low heat

and enabling them to slide over each other under pressure to take up a new form which remains solid on cooling. In other words they are plastic.

The Shape of Large Molecules

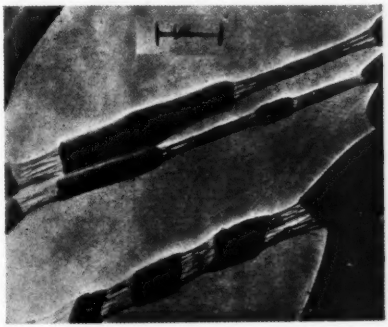
IN spite of these advances we do not yet know much about the exact size and weight of the molecules. In the case of cellulose, for example, all we know is that it is formed of a large number of glucose units joined together. As to the number of these units, some authorities give a minimum of 200, and since the molecular weight of the sugar glucose is 180, the molecular weight of cellulose must be a minimum of 36,000. Other authorities, from physical tests, think it safest to consider cellulose as a thread of 2,000 glucose units (molecular weight 360,000) or more correctly a mixture of long chains of varying length, the 2,000 being the average.

As to what these molecules actually look like we have yet no means of telling. We are, however, on the way to doing so and a recent article in "Chemical Products" (Aug., 1942) on the subject of the electron microscope, by Professor Marton and McBain, is both fascinating and illuminating.

The ordinary or optical microscope has practically reached its limit of resolving. It cannot resolve two points less than 1/50,000 of a centimetre apart. This is small, but it is not small enough for our job.

The electron microscope, which makes use of a stream of electrons in an electric or magnetic field, has a theoretical power of resolving 100,000 greater than the ordinary light microscope. We are getting somewhere!

The electron microscope is now being used to determine the size and shape of particles beyond the reach of the light microscope and to investigate surface phenomena. We are now able to see the small virus particle and what soap curd fibres look like. Of special interest to the plastic industry is the inclusion by the authors of a photograph of polystyrene which has been dissolved in benzene, spread on a water surface and seen through the electron microscope. In it there are two fundamental things to note. The fine filaments are probably molecular chains of the plastic and the dark



Polystyrene under the electron microscope.

clusters are absorbed carbon particles (probably derived from the original raw material of manufacture, benzene). The indication of size—the measure 1μ wide is one-thousandth of a millimetre—would give the fine filaments a thickness of roughly 1/100,000 of a millimetre, that is, about 1/2,500,000 of an inch.

It is also noteworthy that the polystyrene filaments appear to resemble what we have imagined the cellulose micelle or filament to be like. The repetition of the carbon particles at fairly regular intervals is also significant.

We are not yet viewing the molecule itself, but we are steadily wresting Nature's secrets from her.

Shock Resisting Mouldings

IN its natural endeavours to reach a reasonably high ideal the plastics industry has, among other things, sought to produce mouldings with high shock resisting properties normally termed high impact strength plastics. Since the older wood-flour filled moulded fell short of many requirements in the matter of strength, recourse was made

to the manufacture of powders by the mechanical mixture of synthetic resin, e.g., phenol-formaldehyde with cotton flock, macerated fabric or rag. The increased impact strength so obtained is of the order of four to eight times that of ordinary wood-flour material and the powder has now been for several years a standardized article of commerce for the moulder for the production of specialized articles for the engineering and allied industries. It was indeed the first of the phenolic moulding powders to overcome the prejudice of the heavy industries.

Prior to the war there was considerable hope of the large scale production of a new type of moulding material in "powder" and sheet form, made by the treatment of felt or flock with a water-resin emulsion. The impact strengths obtained were considerably higher than those from the flock or rag-filled powders, but its manufacture has unfortunately ceased. It may be pointed out that all the above high strength materials generally have poor flow and are somewhat difficult to mould. These troubles were greatly emphasized when injection moulding was first attempted.

The whole question has come up again with the production by the Plastics Division of Monsanto Chemical Co. of a new phenolic material reported by Whitlock and Haslanger in "Modern Plastics" (June, 1942). In this the fibrous filler is a special twisted cotton cord, chosen after exhaustive tests among a large number of fibrous fillers, including sisal, string, cotton waste, etc.

The results obtained with the new moulding powder are extraordinarily satisfactory. The cord-filled material gives an impact strength some two to three times that of fabric-filled mouldings and some 20 to 30 times that of wood-filled mouldings. It is also important to note that impact strength increases for both cord and fabric-filled materials with rise in temperature, the strength of the former at a more rapid rate than the latter. At about 120 degrees C. to 140 degrees C., while the impact strength of fabric-filled mouldings rises by some 10 per cent., the impact strength of cord-filled material increases by about 50 per cent. This means that at this temperature cord material is nearly four times as strong as the fabric-filled and nearly 40 times stronger than wood-filled on the impact strength test. As for the other mechanical strength characteristics, the ultimate tensile strengths of the three types are about the same (6,700 lb. per sq. in.), but the ultimate flexural strength of the cord-filled material is 13,000-14,000 lb. per sq. in., compared with 11,000-12,000 for the fabric-filled and 9,000-10,000 for the wood-filled samples.

What is also of outstanding importance is that because of the uniformity of the cord employed superior moulding characteristics of the "powder" have been reported—resin segregation is low and flow characteristics improved. This is very evident in view of the statement that the material is readily moulded on injection moulding machinery without destroying the structure of the cord.

Well, I'm Kippered

YEARS ago when we delighted in listening to vulgar conversations and collected slang phrases we once heard the very rare expression "She's well kippered," indicating that a lady in question was well preserved for her age. The derivation of "Well, I'm kippered," meaning "I am surprised," is not very clear, but probably refers to the amazement or indignation of a herring undergoing the smoking treatment.

It is, however, extremely surprising, we shall not say lowering of the dignity of our industry, to learn that the production of synthetic resins probably first began in the prehistoric days when our Yorkshire friends in their smoky caves around Grimsby first accidentally made that toothsome and peculiarly English dish we now call a kipper. But it seems as if it is true, for in a recent paper before the Food Group of the Society of Chemical Industry, Mr. C. L. Cutting of the Torry Research Station tells us that in the preservation of fish by smoking "the products of combustion (of the wood) include formaldehyde and phenolic bodies which, in addition, impart the characteristic flavour of smoked fish and the colour, by the formation of bakelites. . . ." So that no doubt the pedantic and the snobbish will in future refer to the ancient dish as a resin-impregnated herring!

The scientific facts of the matter appear to be that not only do the phenolic bodies and formaldehyde initially kill bacteria, but that the synthetic resin formed by their union is still reactive bacteriologically speaking, and also prevents too great an absorption of water which is necessary for their continued existence.

DETECTION OF CRACKS in Plastic Mouldings and Metals

A New Fluorescent Lighting System Solves a Major Problem

WE need not stress to our readers the necessity of inspection of manufactured engineering materials, and more especially in our own industry, of moulded plastic units. Even in time of peace, whether turning out radio cabinets or cigarette boxes, electrical insulators or textile bobbins, every moulding company great or small has, in some form or other, its inspection department.

The Value of Inspection

If we are to progress on scientific lines we must ask ourselves: What, in fact, do these inspection departments inspect and what is their real value? The inspection department in a moulding factory is, or should be, something equivalent to the testing laboratory in a chemical factory—the arbiter of the quality of the goods sent out. In practice, however, the system, without any special fault of its own, falls lamentably behind the ideal. With the rare exception of electrical testing, or in the case of certain aircraft organic glasses, where the Adam Hilger or other strain tester is employed, scientific methods are conspicuous by their absence. Inspection, other than measurement of size tolerances, is a matter of visual examination—it is true by trained personnel but it is, nevertheless, visual examination by human beings dependent on keenness of sight, on keenness on the job, and on the fluctuating changes of temperament and health that attack us all. Normal inspection other than those enumerated above merely means an examination directly proportionate to the vision of the examiner—of the so-called " finish " of an article, of the amount of " flash," and of obvious breakages. The detection of tiny flaws and hair cracks in the surface is virtually impossible by the human eye.

Methods of Crack Detection

The metal industries, both ferrous and non-ferrous, although so much older than our own, have not progressed as rapidly or as far as one might believe in this respect. The examination of internal faults, blow-holes, etc., by X-ray methods has long been employed, but only in general research work and, we believe, not at all in general production. It is too slow and too costly for normal working. Many methods for the detection of surface flaws have been put forward of which the most successful has been the magnetic one for use with ferrous materials. But no really satisfactory way has previously been devised for the examination of non-ferrous substances, although many have been tried, chief among them being anodizing, and the oil and chalk or dye and chalk methods. Both depend upon the assumption that the crack or flaw can be filled with chromic acid or oil, which, after a time, will seep out and stain the chalk surface in the neighbourhood of the crack.

All these methods have a common base in that they depend upon close visual inspection under a light which illuminates the article uniformly, including the crack or flaw in it. Such inspection demands skilled labour, which is subject to a considerable amount of eye strain. There is an ever-present danger of faulty material being passed as perfect, and, indeed, of good material being rejected as unsuitable.

On August 27 we were permitted to view a demonstration of an entirely novel process for the examination of metallic and non-metallic manufactured units—one that promises to be an important new tool in the hands of industry.

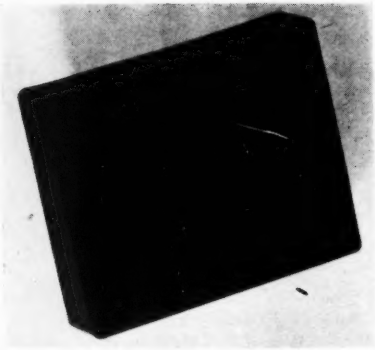


Fig. 1.—Plastic box lid treated by the Glo-Crack process and photographed in u.-v. light. The crack shows as a luminous line.

The system, known as " Glo-Crack," has been introduced by Colloidal Research Laboratories, Ltd., of 66, Petty France, London, S.W.1, and is a development of the B.A.B. system of fluorescent lighting which we have already described (" Plastics," Feb., 1942) in general terms.

The use of ultra-violet light and fluorescent materials offers a new approach to the problem. A non-fluorescent material illuminated with ultra-violet light will appear black or purple, depending upon the nature of the material; a crack or flaw in that material, if filled with a fluorescent filler, will glow with a characteristic colour—in effect, the crack or flaw is filled with light, while the remainder of the specimen remains dark.

The advantages of such a method are too obvious to need enumeration.

The " Glo-Crack " system makes use most successfully of this phenomenon. The specimens, pressings, stampings, etc., to be examined are immersed for an automatically controlled period in a bath of fluorescent material at a temperature of 75 degrees C. The specimens are withdrawn and then washed in a cold solution which removes all fluorescent material that has not become anchored to the edges of the flaws or cracks.

Examination under a " black " lamp (a source of ultra-violet light) immediately shows up any flaws or cracks. Surface scratches which have a depth only equal to, or less than, their width, are not shown. The total time taken to examine in this way a large specimen, such as a piston, does not exceed three minutes. The method is both speedy and certain.

The exhibit included a small but full-scale plant of the single batch or tray type. It consists of two tanks, one for the electrically heated thermostatically controlled solution of fluorescent material, and the second containing the cold washing solution. The total floor space of this model is about 3 ft. by 6 ft., the current consumption being of the order of 1 kw. The throughput, however, can keep pace with any production line. The method is simple and labour can be trained in a few hours.

In addition to the batch type, models are available utilizing conveyors for continuous processing, the operation being entirely automatic.

Variation in Technique

The shape of the articles governs to some extent the technique employed—for instance, articles which can be loaded into trays and handled in batches can be best processed by dipping. Larger

Fig. 2.—Bronze-lined bearing showing bad adhesion between liner and steel housing, continuing as a crack in the liner.

articles, such as airscrew blades, need a different technique. In general, the process can be adapted to deal with any articles, and has been successfully employed on specimens ranging from contact-breaker screws to aircraft petrol tanks.

Raw Material Loss and Cost of Processing

The materials which are the core of the system are organic solvents which efficiently perform their primary function of maintaining the fluorescent material in solution and of carrying it into the flaws or cracks. They also efficiently and thoroughly degrease any specimen immersed in them.

The fluorescent treatment loss is approximately .23 gal. per 1,000 sq. ft. of specimens, and the washing solution loss approximately .17 gal. per sq. ft. At the prices ruling to-day, this works out at under one penny per sq. ft. treated. In a continuous plant further economies can be effected by the addition of solvent recovery plant.

Since we were invited to bring our own faulty specimens, we were allowed to treat a moulded cover plate made of phenol-formaldehyde resin, the base of which we had carefully cracked so that the split was quite invisible to the naked eye. The result is shown in Fig. 1, where the crack is readily visible.

Plastics for Plumbing

In the far-off days of piping peace, when the vinyl chloride and other somewhat rubbery polymers were first extruded into tubes, most of us immediately translated this advent as a means of entering one of the toughest of trades—that of plumbing. Indeed, rumours had it and photographs proved it that polyvinyl chloride tubing of the hardish variety was being employed to convey beer from the cellar barrels to the counter bar. This had happened in Germany, but we had forebodings that any attempt to sell plastic tubing to British publicans instead of copper or glass would get a frigid reception. Tentative suggestions had been put forward, too, for the production of similar plastic piping for water supplies and water-wastes. One very strong argument in its favour was its use in soft-water districts where attack on lead piping has been known to induce lead poisoning. The restricted production of such plastics in war-time has no doubt forced the shelving of such problems.

In the U.S.A., where metals are now as short as anywhere else for non-military work, the problem of plastics for plumbing is, however, being energetically examined. "The Scientific American," of August, 1942, reports the successful manufacture and use of a new flush elbow for connecting the tank with the water closet. It is described as "a one-piece moulding in tough resistant plastic, by the American Molded Products Company. The new 'L' provides strength with lightness; it does not break, crack, or dent in the usual packing and handling with tools. It is stated to be leak-proof, impervious to water or to iron, lime, sulphur, salt, or other water-carried material, and to be non-corrosive. It is made of a porcelain-like, white, odourless plastic with a smooth finish inside and out."

Stamping Nylon Fabric to Form

A novel method of forming wearing apparel from nylon fabric by stamping, in a way resembling the shaping of sheet metal, has been invented by Vernal R. Hardy, of Wilmington, Delaware, to whom has been issued a United States patent assigned to E. I. du Pont de Nemours and Co. The process, according to the patent specification, would increase the production rate and reduce the cost of such feminine wear as brassiers, girdles, foundation garments, gloves and hats made of the silk-like fabric. The inventor claims that it would also result in better fitting and no seams.

In a description of his method, the patentee states that he uses fabric woven of nylon yarn which has not been "cold drawn," or stretched, to increase the fineness and strength of the fibres, or that has been only partly so treated. A cut-out blank of the fabric is clamped between male and female dies having the contour of the article to be formed. Clamping pressure draws or stretches the fabric to the die shape, and heat applied to the dies through the medium of steam or a hot liquid sets the piece of fabric permanently to form.

D

PRESSES for PLASTICS

Presenting a Comparative Study of the Design and Use of Mechanically and Hydraulically Operated Equipment

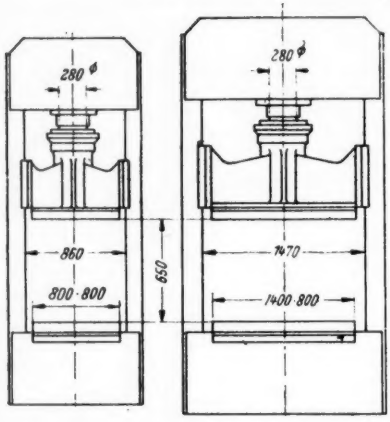


Fig. 1 (left).—Standard down-stroke hydraulic press; table area 32 x 32 ins.; weight about 5 tons. Fig. 2 (right).—Standard down-stroke press; capacity as in Fig. 1 but with table 64 x 32 ins.

IN spite of the universal use of either mechanically or hydraulically operated presses for moulding plastics, little has been published regarding the limitations of either system of construction. For this reason, interest attaches to a review of the present state of development in this special field recently contributed by H. Van Hüllen,* a prominent Continental manufacturer of large hydraulic presses.

The capacity of presses for plastic moulding is determined by the specific pressure required for deformation and hardening of the plastic material, this factor depending on the type of plastic employed and on moulding temperature.

Presses up to 10,000 tons capacity have been constructed, the size of the press to be used for any particular work depending ultimately on the size of the moulding and the mould used.

For example, the 150-ton press, shown in Fig. 1, has a table area of 32 ins. by 32 ins. If a total pressure of 42,000 lb. be required, the press can be used with a mould of 77 sq. ins. in area. Obviously, however, such a mould could not be located in the limited space between the uprights; the maximum dia. would be about 10 ins. Therefore, the capacity of 150 tons with a ram dia. of 11 ins. would be more fully utilized in a press with a greater table area, namely, 64 ins. by 32 ins., shown in Fig. 2. Such a press can take moulds for components up to 77 sq. ins. in area.

This example shows that, besides the capacity of the press, its essential dimensions must also be considered. The fact that in the second case the table surface is larger implies that the machine itself is heavier, its weight, in fact, being increased from 5 to 7 tons.

The height of the component being moulded must also be taken into account, hence working space between the opposing surfaces of ram and table must be adjustable within wide limits. General accessibility is important. When charging moulds with the usual moulding powders front access is, as a rule, sufficient, whereas where fibre-filled masses (which do not flow well and which, therefore, must be inserted into the mould in a preformed shape) are concerned, it is desirable to have access to the mould from all sides.

The moulding process is influenced by the flow and hardening characteristics of the plastics in the mould (Fig. 3). The operation cycle is periodic, periods for charging, closing, opening and removing being auxiliary times which should be cut

* "V.D.I. Zeitschrift," 1942/86/231.

down as far as possible. It is important that during the actual hardening (e, Fig. 2) the pressure remains constant so that the press can adapt itself to the conditions as given by the ranges b, c, d.

According to construction and principle of action, presses may be classified as hand operated, mechanically driven or hydraulically operated.

Hand-operated presses are built up to pressures of 80 tons. In the range between 20 and 500 tons mechanical presses with motor drive are commonly employed. For

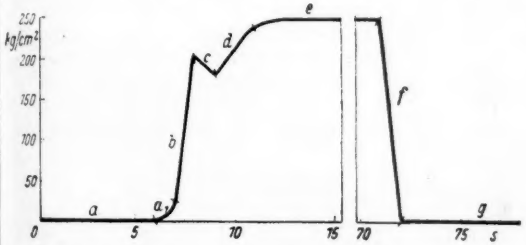


Fig. 3.—Curve of pressure in mould charged with plastic moulding powder: a, mould closing (no pressure); a_1, transition to low pressure; b, cold compression and distribution, with heating of plastic mass (high pressure); c, softening of the mass; d, plastic deformation of mass; e, hardening of mass; f, release of pressure; g, opening of mould.

still greater pressures and for longer strokes, the dimensions of a straightforward mechanical movement become unwieldy, hence hydraulic systems are used.

For these presses, water or pressure oil supplies the piston movement. The hydraulic press is favoured for pressures above 300 tons, but may be used equally well for smaller capacities as no transmitting gears are incorporated and it is possible to obtain large strokes. Because of this, hydraulic presses are used for the moulding of tall components demanding a long compression stroke; the actual high pressure which an hydraulic press may yield, may not be necessary.

Mechanical presses in the range referred to are advised for the mass-production moulding of small flat parts. In mechanical presses, power to the ram is transmitted by crank, toggle levers, double crank levers or roller-cam teeth. These mechanisms are suitable for the moulding of plastics in so far as the compression stroke is initially rapid, pressure increase being thereafter slower.

In the case of crank drive, speed, which is at a maximum when the crank nears the horizontal position, drops to nearly zero at the end of the stroke. For the same applied torque, pressure would increase infinitely until dead-centre position of the crank was reached; however, in practice, this force is limited by the load

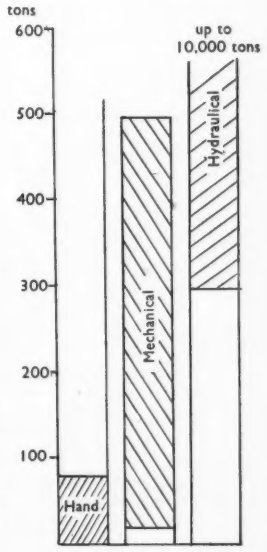


Fig. 4.—Comparison of range between hand-operated, mechanical and hydraulic presses.

which can be taken by the press supports.

In the straight-line position of crank and connecting rod, the end pressure during hardening time is exerted. Thus, the ram must be in its end position when the mould is fully closed, and for various heights of mould, either table abutments or ram have to be adjusted.

Height adjustment must be carried out with extreme care so that the press reaches its full capacity, but at the same time is not overstressed. The mould, too, must be preserved from overloading due to faulty adjustment.

In the case of the usual crank drive it is only during the last $\frac{1}{16}$-in. motion before reaching end position that a great increase of pressure takes place, hence for the deformation of a given mass in any one mould, working time is short, whilst the working movement of the crank may also be regarded as very limited.

The time available is sometimes insufficient for causing adequate flow of the moulding powder. Instead, therefore, of the single crank, double-crank levers, double-toggle levers or roller-cam teeth are used, in which pressure increase is distributed over a longer crank path.

With roller-cam teeth it is possible to obtain end or maximum pressure before the lowest position of the ram, this pressure then remaining constant to the end of the stroke. In addition a quicker return speed is obtained.

From a theoretical standpoint, the mechanical press seems to be ideal for plastic moulding insofar as initial application of pressure is rapid, speed of application then dropping rapidly with great increase in applied pressure, that is, the flowing characteristics of the mass are catered for; constant end pressure being attained at the end of the stroke, after which there is a slow return from the mould and, ultimately, quick return to lift the upper portion of the mould.

The disadvantage of mechanical devices, however, is that the press operates till end pressure is obtained in periods of time fixed by the design of the mechanism. Thus, with non-uniformly filled moulds, or with an unplasticized mass, overloading of press and mould may occur.

The difference between the pressure-course required by the mass and that provided by the press itself can in the

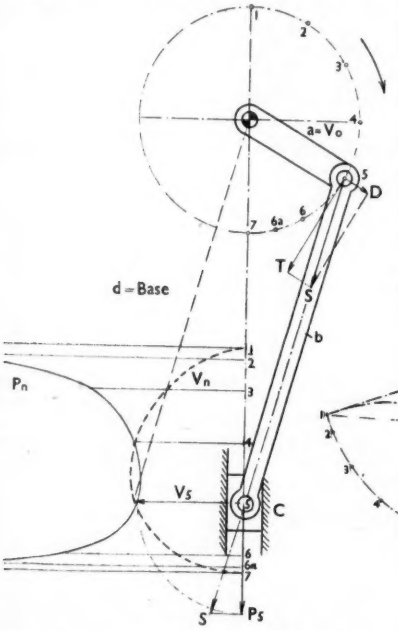


Fig. 5 (above).—Scheme of crank mechanism used in plastic presses together with velocity and pressure diagram.

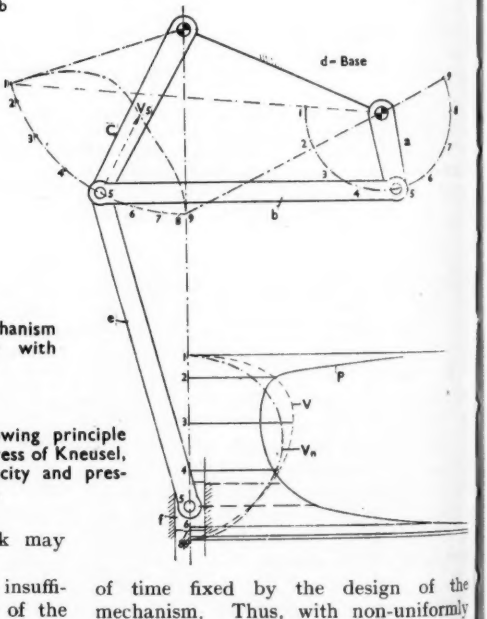


Fig. 6 (right).—Diagram showing principle of the double-toggle lever press of Kneusel, together with relevant velocity and pressure diagram.

case of hand-operated presses be balanced by moving from stage to stage, a process not possible, however, in the case of motor drives which, for this purpose, require a flexible transmitting member between drive and ram in order that torque exerted by the motor be equated to the requirements of the moulding process. The most primitive device of this type is a slipping clutch, which is, however, subjected to high wear owing to its frequent operation.

Oil-operated hydraulic slipping clutches are more satisfactory as, simultaneously, they allow the total pressure of the press to be changed. Another solution is the operation of the double crank by means of oil, hydraulic or pneumatic pistons.

No adequate analysis has yet been published of the mechanisms employed in the various types of mechanically operated presses. For this reason it is proposed to present here a comparative geometrical analysis of such devices with special regard to velocities and pressures.

It is comparatively easy to determine ram velocity if the rotating speed of the driving member be known, but pressure analysis is somewhat complex. This problem is rendered easier if the relationship $N = c \times P \times V$ be employed, where N = capacity in h.p.; P = applied pressure in lb.; v = speed in ft./min. and c = conversion factor of 1/33,000, as V and N are known, N being usually constant, P may be calculated from

$$P = \frac{N}{c \times V}$$

Fig. 5 shows the ordinary crankdrive and its analysis when used as a mechanism for presses. The crank arm (a) is connected by the rod (b) with a ram (c) running in vertical slides. The stroke, 2a in length, is performed during a movement of the crank through 180 degrees. The downward stroke is performed when a describes the half circle 1 to 7.

The actual velocity of the ram may easily be found by dropping a perpendicular to the line of motion of the ram and a parallel line to the connecting rod through the crank centre. The assumption is made here that the length of the crank arm is equivalent to the velocity of the crank. In this way, as shown for point 5, the velocity curve V5 is obtained.

The pressure P may be obtained by using the relationship given above, and

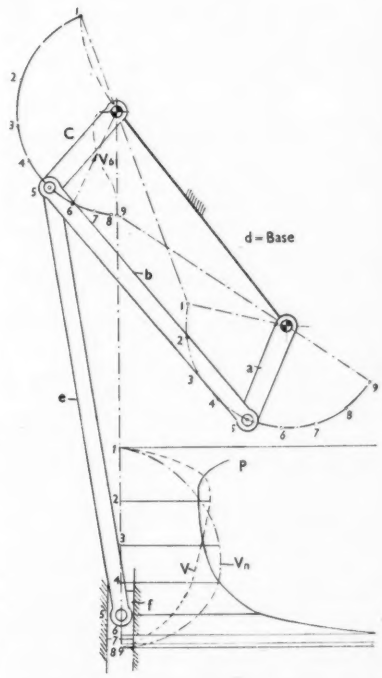


Fig. 7.—Double-toggle-lever press with swinging arms of equal length (the "double crank" press of Gebr. Goetz) with relevant velocity and pressure diagram.

by graphical method involving the distribution of the tangential force T into force S falling in the direction of the connecting rod, and a force D.

The dimensions of this crank press, and the course of Vn, were used as bases of comparison for the other press mechanisms investigated.

In the crank press of Kneusel (Fig. 6),

the crank does not act directly through the connecting rod to the ram, the connecting rod (e) being connected with the swinging lever of a four-bar line (a, b, c, d). The crank (a) of this system cannot perform a full rotation, its angle being limited to approximately 210 degrees.

In contrast to the crank drive illustrated in Fig. 5, Kneusel's gear has two toggle dead-centre positions. In the moulding position 9, members a and b are superposed and members c and e are in the extended position (double toggle lever). Simultaneously, in position 1, members a and b are in an extended position.

From these data may be designed mechanism to give a predetermined stroke. Ram velocity (V) is determined geometrically, and the speed to the end point of the swinging member (V, c), together with the velocity curve of the crank mechanism (Vn) are also introduced. Comparison between V and Vn indicates that the ram obtains the highest speed in the first quarter of the stroke, velocity being subsequently more rapidly reduced, the velocity curves intersecting in the last quarter of the stroke.

The double-crank presses of Gebr. Goetz (Fig. 7) utilizes a similar mechanism, only in this case a and c are of the same length, hence the term " double crank "—a somewhat misleading terminology, as the co-called " cranks " do not perform full rotations. Crank a is driven, and drives, by means of connecting rod b, the second crank c, the length of which differs from the actual centre distance of the crankcase.

The main connecting rod e is linked at the same point. The course of operation in relationship to velocity Vn, is similar to that shown in Fig. 5. Maximum speed is reached after an interval of 20 per cent. of the total stroke, whilst beyond 30 per cent. of the total stroke speed is below Vn.

In Grefe's press (Fig. 8), a toggle-lever press, drive is by means of a four-bar linkage (a, b, c. d). In this case

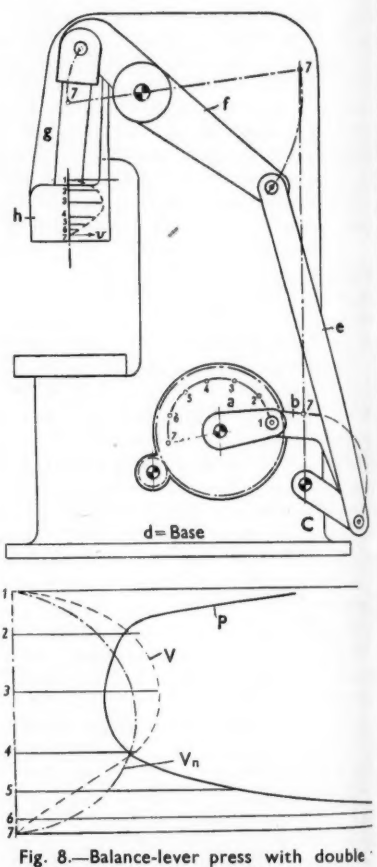


Fig. 8.—Balance-lever press with double toggle transmission, according to system of Grefe, together with relevant velocity-pressure diagram.

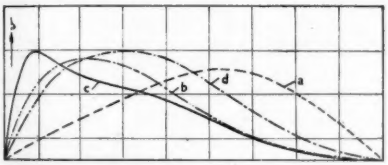
also the crank does not make a full rotation, being limited to a movement of 180 degrees. Crank (a) operates swinging lever (c), by means of a bell-crank connecting rod (b). Swinging lever (c) drives the main connecting rod (e), which operates the balance lever (f). The ram (h) is operated by connecting rod (g).

In the closed position, 6, members a and b are superposed, whilst c and e are in the extended position. By comparing the velocity of the ram, Vn, it is

obvious that V is higher for about two-thirds of the stroke, but the positions for maximum V and maximum Vn are practically the same.

A notable feature of this mechanism is the approximate linear decrease in speed, indicating a corresponding linear increase in pressure.

Better to compare the various mechanisms, the velocity of the ram and ram pressure are plotted in relationship to the angular positions of the driving member at any given time (Fig. 9). Similar



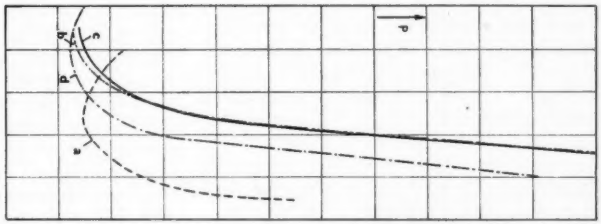


Fig. 9 (above).—Velocity-time curves for presses. Fig. 10 (right). — Pressure-time curves for presses: a, crank press (Fig. 5); b, double-toggle-lever press (Fig. 6); c, double-toggle-lever press (Fig. 7); d, balance-lever press (Fig. 8).

curves to those shown in Fig. 9 are obtained when velocities are plotted in relationship to stroke. As regards pressures, these are best plotted in relationship to time. (Fig. 10.)

It should be noted that in this analysis no attempt has been made to consider the possible influence of elastic-reaction devices to increase effective stroke.

Single-pillar presses suffer from the disadvantage that the press frame is subjected to bending forces which tend to cause mal-alignment of the mould halves. With presses of higher capacity, therefore, closed frames are almost exclusively used, the uprights being stressed in tension only.

Such machines are built up to 500 tons capacity and with strokes up to 20 ins.

Ejectors are either hand-operated or mechanically connected with the returning ram. In the case of hand operation, rack and pinion movements or other mechanisms are employed.

To facilitate operation and to stop the motor when the end of the stroke is reached, electrical controls, preferably of a push-button type, are used. An adjustable time control is incorporated to start the motor again for the return movement. An emergency control button is provided for quick return where it appears likely that excessive stresses would be imposed on the mechanism. This emergency unit can also be used to control the pressing operation step by step, when complicated mouldings are being made or where systematic filling of the mould has not been obtained.

Hydraulic Presses

With hydraulic presses (Figs. 11-14), effective pressure is independent of the position of the ram, hence moulds of various heights may be used without special adjustment of the press.

Owing to the fact that in fluids pressure may be built up at will, it is possible in hydraulic presses to effect full pressure over the whole of the press stroke at constant speed, and total pressure may be maintained at any point in this stroke.

Rapid approach is obtained by quick-acting cylinders operating in conjunction with pre-filling cylinders and return cylinders. Valves controlled from the press table enable pressure to be regulated according to the reaction of the mass in the mould.

It will thus be seen that the working requirements of plastic moulding are better catered for by the hydraulic press than the mechanical press.

The pressure capacity of the main piston equals the product of piston area by fluid pressure per unit area. For service and safety reasons, fluid pressure is limited between about 10-20 tons/sq. in. Pressures in excess of this result in excessive wear of valves and pump mechanism. Pressures below the lower limit, again, are not used, as the press mechanism has to be made so large as to become unwieldy.

In order to save high-pressure water, it is customary during the closing stroke for the cylinder to be filled with water which flows by gravity from an overhead container, or is taken from a special low-pressure accumulator operating at 35-225 lb./sq. in. High-pressure water is used only for the actual moulding process proper. The speed of approach of the piston depends entirely on the inlet-valve cross-section.

The mould is opened by a special return piston with a capacity of 15-30 per cent. of the main piston. Some manufacturers use high return pressures in order to facilitate the withdrawal of sticking or seized moulds.

Return pistons may be constructed as differential pistons; this gives compact design of press, but suffers from the disadvantage that, after long use and by reason of leakage, pressure may be reduced without being detected. In general, therefore, return pistons connected by bars and traverses with the table are preferred, even though this means increase in the structural height of the press. This latter disadvantage may be eliminated by replacing the central return cylinder by two cylinders arranged at the sides of the main cylinder.

The connecting bars are threaded and provided with double nuts which come into contact with a stop on the upper crossbar; in this way, the total stroke may be only partially used and high-pressure water saved.

Return cylinders are, in nearly every case, operated with high-pressure water in order that their size may be reduced to a minimum. In order to simplify control, the return piston is sometimes maintained continually under pressure, this having the effect of reducing working pressure by an amount equal to the maintained return pressure.

Great care in design is necessary for hydraulic presses. Applied loads should not be unduly high, or deformation of the structure by bending or extension beyond the elastic age may occur, and this in the case of big presses may entail high-pressure water consumption above that required for the production of the moulding itself. Press table and crossbar should not be subjected to great deflecting loads, otherwise the operation of the mould may be adversely affected.

A further point to be observed on a press construction generally is the protection of the press parts against conducted heat from the mould. Thermal-insulating plates of high compression strength, or devices incorporating cooling plates, should be used.

As the main press elements, that is, piston and cylinder, in the hydraulic press are simple in design, it is possible to construct presses which give pressure in any desired direction, and to combine several pressure elements. Thus presses with downward stroke are commonly used for simple steel moulds, whilst presses with a vertical main piston and one or two horizontal closing pistons are suitable for mouldings with undercuts. For moulding laminated materials or for preparing mouldings with metal inserts in hand moulds, presses with upward stroke are useful.

Downward-stroke presses are constructed with movable or stationary cylinders. The advantage of the moving cylinder lies in the increased guiding length available, as practically the whole cylinder length may be utilized for this purpose. Moreover, as the sealing is at the top, no sediment from the pressure water can come between piston and cylinder surface (Fig. 12).

The use of oil in hydraulic presses is largely limited to small units and to those with rotary pumps, which operate satisfactorily only with oil. Adhesion of oil to the ram of an hydraulic press implies that,

for every stroke of the piston, " drag out " losses occur, and care must be taken to return oil so lost again to the circuit. In big hydraulic plants operated by oil, leakage may lead to explosions, as the oil ejected may be highly atomized.

For economic reasons, a large plant is commonly not operated with oil; trouble due to leakage and to creep may cause

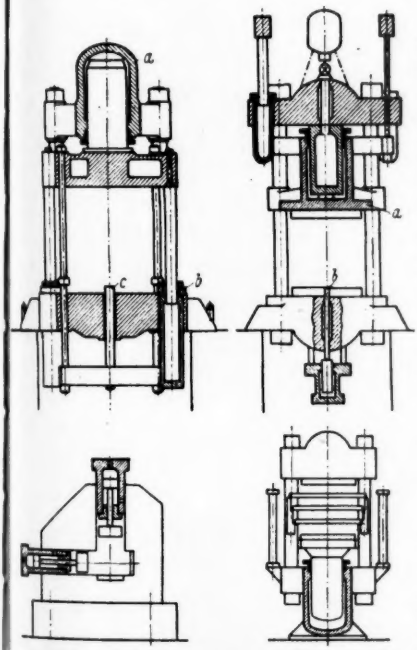


Fig. 11 (above, left).—Down-stroke press with stationary cylinder (a), hydraulic withdrawal from below (b), ejector in connection with hydraulic withdrawal (c). Fig. 12 (above, right).—Down-stroke press with moving cylinder (a) and hydraulic injector (b). Fig. 13 (below, left).—Angle press with hydraulic withdrawal (differential piston). Fig. 14 (below, right).—Up-stroke press.

moulding powders to become contaminated.

In general, water is a more convenient medium, rusting of the press parts being suppressed by addition to the water of suitable inhibitors. Furthermore, with water there is no danger of gumming up or of attack on packing material and gaskets. Owing to the fact that suspended foreign matter in the water may lead to breakdown or leakage of valves, regular filtering is advised.

For generating the required pressures, two- or three-stage pumps are used, which, in the case of presses of the largest capacity, entail the use of motors of up to 3,000 h.p. They are of the low-speed type in this case. For smaller plant, high-speed pumps operated by 10-20 h.p. motors are used.

A distinction is made between presses driven by integral hydraulic units and between those of the group-drive type used in combination with accumulators. Single press units are practicable for small plants as one or more can be put into operation, according to the amount of work in hand, whilst difficulties due to breakdown are confined to one machine only. Where a large number of such units are used, however, separate drives become uneconomical, both in operation and maintenance, and group drive with hydraulic accumulators is preferable.

The capacity of accumulators is to be determined on the assumption that, it necessary, all presses can work simultaneously, although this condition will not often have to be met. The capacity of driving pumps is determined by average hourly pressure-water requirements.

In the case of unit drive, motors must be of the capacity demanded by maximum requirements, hence, for a battery of presses, the total capacity to be catered for is greater than that required where a group-drive system is employed.

For large presses, the provision of a pressure accumulator effects considerable economy. For example, an 8,000-ton press operating under any given working conditions requires a 45 h.p. drive in conjunction with a pressure accumulator, whilst for direct pump drive 420 h.p. is necessary.

Another advantage gained by group drive is that only one or a few pumps are required, maintenance and supervision being confined to these; the accumulator

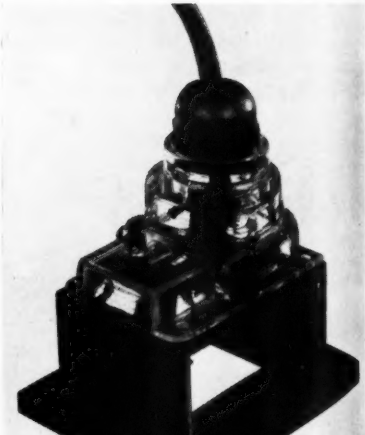
(Concluded on page 315)

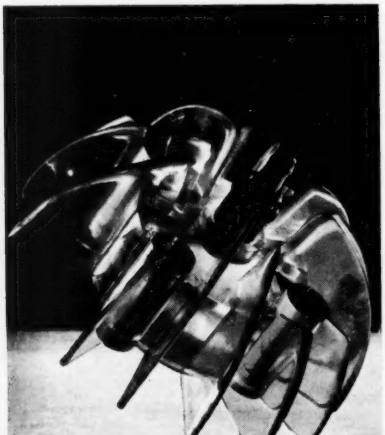
TRANSPARENT MODELS for Engineers

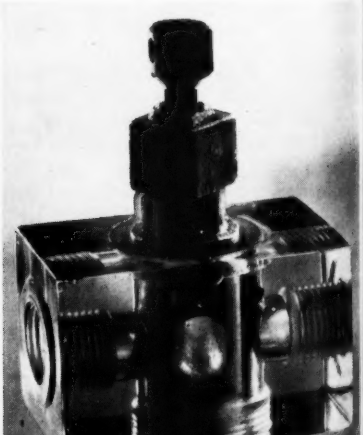
AS our military correspondents might say, progress is being maintained on the transparent cast resin front and breaches are being widened in the engineering industry.

We shall not say that the production of engineering models made on the principle of "see how it works" has become a major industry, although judging from the publicity we have given the subject during the past year or so the unwitting might consider it so. The number of concerns that are wide-awake enough to see their possible uses and have taken advantage of them can be counted on the fingers of, say, four hands. However, as we have already said, progress is being made and we are grateful to Runcolite, Ltd., who made the models, for the accompanying photographs.

They show (on right) a selector system for the Ford gearbox and (below) a cylinder head with cooling fins and a piping system with valve. They portray very admirably how useful such models are in the teaching of engineering science as well as in the improvement of design.







World's Industry Employs Plastics

BUILDING

Sealing of tunnels against penetration of water and diffusion of water vapour appears to have been achieved by means of certain polyvinyl-chloride materials. Theoretically, the older method of placing the sealing layer on the outside of the tunnel lining was the more satisfactory, but introduced practical difficulties. The use of waterproofing layers on the interior surface, on the other hand, was coupled with the danger of excessive moisture on the outside of the tunnel diffusing through and forcing the layer off. A part solution was found in the enclosing of the waterproofing layer between two rigid walls, but this expensive system may apparently be dispensed with, polyvinyl-chloride mixtures having been evolved which may satisfactorily be applied to the interior of walls and which resist mechanical separation from the structure. **Peat consolidated by means of synthetic resins** is said to have been produced by a concern in Warsaw and is claimed to have proved an effective substitute for cork for thermal insulating purposes. **Properties and uses of so-called "Homogenholz"** were discussed before a recent meeting of the special committee on wood problems of the V.D.I. The material itself consists of organic fibres impregnated and bonded by means of synthetic resins. Unlike natural wood, it is mechanically isotropic and may be worked and handled precisely like wood. Homogen board of S.G. 0.5-0.6 is suggested for use in furniture and interior woodwork, whilst that with an S.G. of 0.8-1.0 may be used for flooring, for rolling stock and shipbuilding work and stressed parts of furniture.

TEXTILES

Electric spinning process for direct production of textile fibres of acetyl cellulose is described by Werner in "Chemiker Zeitung," 1941/65/389. The spinning solution consists of 15 per cent. acetyl cellulose in acetone-alcohol. This is forced under low pressure through spinnerets. The viscous thread which emerges passes into a receptacle connected with one electrode of a high voltage source, the other electrode being situated at a distance of 1.1 yards from the jet opening and 0.66 yard to one side of the jet. Under the influence of the electric field, the fluid strand separates into numerous fine filaments. On evaporation of the solvent these filaments acquire a powerful electric charge and are attracted at high speed towards the wire electrodes. The ionized atmosphere in the neighbourhood of these electrodes is sufficient to neutralize and reverse the charge on the strands before any contact is established. They remain in the air distributed in a high state of uniformity and may easily be removed. The discharge gap acts as an automatic high tension switch as the electric field breaks down periodically. The thread generated is said to be very suitable for spinning and to resemble, in some respects, wool. It is very durable mechanically and a bad conductor of heat. The electrical system described here appears to be generally applicable to fibre production from viscous solutions of the type described and would, furthermore, lend itself to modifications in current practice leading to improvements.

ELECTRICAL

Function of both insulator and protective conduit is assumed by latest plastic development; saving effected by this is made clear by the following details. Principally it is to be noted that electrical wiring for household and industrial use can now be in the form of bright uninsulated wire; necessary protection and safety being conferred by the plastic tube. Tubes are of circular cross-section and contain two or more bores of sufficient size to allow easy introduction of the conductor, giving sufficient clearance all the way round, adequate ventilation of the channel, and space for the wiring to expand. The bores may be circular or sector shaped, although the circular form is recommended as giving the highest mechanical strength. Tubes are made of wood-flour-filled phenolic resin for smaller sizes. Larger installations require the use of porcelain. Plastic insulator tubes are designed for use in dry surroundings and are produced for conductors of 2, 5, 6, 16, 35 and 70 sq. mm. cross-section and in lengths of 3.3 and 5.5 yards; a specification (VDE o288) has been drawn up giving recommended dimensions, weights and cross-sections. Elbows, bends and other accessories have been designed for use in conjunction with the plastic tube. Connections between straight runs and elbows are effected by sockets. For smaller cross-sections this system is somewhat more costly than the ordinary system of insulated wire, but it is interesting to note that the wire can sustain a higher electrical load than rubber-insulated conductor as the tubes themselves and the arrangement of the wires in them confer higher electrical strength as well as greater resistance to sudden or prolonged heating. Wires so run may safely be operated at a uniform temperature of 100 degrees C. Experiments have been carried out since 1937-8 in various localities with transmitting capacities up to 500 kilowatts and with systems involving a total of 29,000 yards of resin tubing and about 110,000 yards of bare aluminium conductor of cross-section up to 70 sq. mm. Among the situations explored were a barrack-room floor and a school building; in both cases results were satisfactory. There is no doubt that the use of insulating conduit is particularly advantageous in so far as it gives perfect contact protection. Further details will be found in an account by Wandell, Kunststoff Technik, 11, 1941/193. **Electric fan guard** produced by Westinghouse Co. has moulded Lumarith centre boss. It is manufactured by Bryant Electric Co. Quite apart from the decorative effect achieved, it is pointed out that the change over to plastics saves metal, reduces the weight of the fan and eliminates noise due to vibration. **Non-kinking telephone cord in extruded Tenite II** and ethocel is being manufactured by the Keystone Rubber Co.

AIRCRAFT

Oil - gauge glasses used in a medium bomber now being produced in U.S.A. are injection moulded in an acrylic resin (Crystalite). The high production speed for this component, coupled with the fact that it retains its transparency indefinitely, is resistant to the effects of flowing oil and high impact strength are alone sufficient to recommend it for this war-time need. **Moulded plastic plywood,** according to U.S.P. 2,276,004, is finding increased use in aircraft construction, and an account in a recent issue of "Modern Plastics" details the Vidal method of moulding by hygrostatic pressure. This system, which has been used before for small articles and forms the subject of a patent for hard-metal pressings, has been applied by Vidal for moulding fuselage parts.

SHIPBUILDING

Marine instrument dials, cut from $\frac{3}{16}$-in. catalin sheet, finished matt, are being produced by Plastic Turning Co., Inc. Pointers are also being produced from the same material and machined to shape. This material possesses the necessary shock resistance to resist the influence of gunfire, is translucent and thus simplifies illumination for night reading. Compasses in transparent lucite cases moulded by the Chicago Moulded Products Corp., are now being used for training purposes in naval academies in U.S.A. On small compasses the plastic cover is adapted as a magnifying-lensing, top and side visibility are equally good. It is pointed out that the material does not discolour through handling or exposure to saline atmospheres and in contrast to brass and glass is far less easily broken or dented.

GENERAL ENGINEERING

Laminated plastics on textile bases have been made subject to restrictions in Germany. Since April 13, 1942, sheet, tube, bar and section came under the new ban. Where such plastics replace metal in bearings, parts of bearings, such as collars and segments, slideways and military equipment, their use is permitted. They may also be used where it can be demonstrated that they definitely replace non-ferrous metals, where their use is essential for damping vibration, and where applied load is such that plastics with macerated textile or cellulose material could not be employed. Spur gears and wormwheels, otherwise in metal or rawhide, and demanding vibrationless, noiseless running may also be manufactured in laminated plastics. Other uses taking advantage of high moisture resistance of this material and its low tendency to swelling, its high resistance to chemical attack, low notch sensitivity and resistance to speed are also still permitted provided that laminated paper plastics and laminated impregnated wood cannot be used. It is significant that this new order does not except military objectives or goods for export ("V.D.I. Zeitschrift," 1942/85/350). **Non-metal running in non-metal bearing** forms the subject of B.P. 544,800 granted to Landis and Gyr, Zug, Switzerland. Both the bearing and the part which runs in it are in plastics. Thermo-plastics and rubber are both referred to and the patent covers also a thrust bearing. **Conversion from peace-time to war-time requirements** is dealt with by Lougee in the July issue of "Modern Plastics." The account presented deals specifically with the manufacture of eye-pieces in cellulose acetate for gas-masks. It is interesting to note that acrylics were first suggested for this use, Chemical Warfare Service finally specifying the acetate, however. Particular attention is devoted to the reorganization involved in the production change over, the bulk of the account dealing with the manufacture of the lenses.

FANCY GOODS

Vegetable flour-filled urea resin solution suitably coloured is suggested by Carlo Enrico Bezzoni, of Milan, Italy, in Italian Patent 366,221, for forming a very suitable medium for modelling. It is said to machine with particular ease. **First-aid for headaches,** popular in U.S.A., appears to be an ice-bag made in suitably decorated waterproofed textile material provided with a Durez moulded cap with integral threads. The cap is easily gripped and will not corrode or stick.

FILLERS FOR PLASTICS *(Contd.)*

Information regarding the effect of fillers on the properties of mouldings, etc., is essential to future development of the industry. In this continuation of his article the author deals with the properties of wood flour, cotton, silk, paper and asbestos

By
E. E. HALLS

[Editor's Note: Owing to lack of space in the August issue of "Plastics" we were compelled to hold over two tables which belong to the introductory section. In tables Nos. 10 and 11 are shown test data appertaining to the moulding powders of the thermosetting (phenolic) and thermoplastic (benzyl cellulose and cellulose acetate) types.]

Wood Flour

WOOD flour is the most important of the plastic fillers, meeting the requirements of availability in plentiful quantities of consistent quality and being reasonably inexpensive. It must not be confused with the sawdust filling of commerce which performs the useful function of packing voids in toys and other articles of domesticity. Wood flour, or meal as it is often termed, is finely pulverized wood of selected origin. Provided the qualification "selected" is borne in mind, there is no objection to the use of wood waste such as sawdust, off-cuts and the like being used in its manufacture. Various grades of wood are usable, but the soft varieties are most favoured, and European wood flours are usually from the spruce, white pine or fir species. They yield white flours, an important point especially for pale-coloured plastic products. The minimum content of resinous matter natural to the wood is an essential because, obviously the effects of such a constituent will modify the properties of the plastic with which it is ultimately incorporated. Thus the long-leaf yellow pine is avoided. Cleanliness is another feature of first

Table 10.—Characteristics of some Typical Thermosetting Moulding Powders (Phenol-formaldehyde Type).

Sample No.	1	2	3	4	5	6
Colour	Brown	Grey	Black	Black	Black	Yellow
Analysis—per cent.:						
Phenolic resin	49.5	38.0	53.5	53.5	60.5	35.0
Wood flour (dry basis)	37.5	41.5	35.7	39.5	32.0	Nil
Moisture	4.5	4.0	4.3	5.0	5.5	1.0
Mineral pigment or filler	8.5	16.5	6.5	2.0	2.0	64.0
	100.0	100.0	100.0	100.0	100.0	100.0
Nature of colorant	Oxide of iron	Carbon black	Spirit soluble dye	Spirit soluble dye	Spirit soluble dye	—
Nature of mineral matter	Oxide of iron	China clay	Oxide of iron	—	—	Clay
Specific gravity of moulding powder	1.17	1.23	1.15	1.20	1.15	1.28
Particle size—per cent.:						
Retained on 20 mesh	30	4	30	30	25	5
Passing 20, retained on 40 mesh	30	32	30	35	30	25
Passing 40, retained on 100 mesh	20	34	20	20	25	30
Passing 100, retained on 200 mesh	10	16	10	10	10	25
Passing 200	10	14	10	5	10	15

Table 11.—Characteristics of Some Typical Thermoplastic Moulding Powders (Cellulose Acetate and Benzyl Cellulose).

Type	Cellulose acetate						Benzyl cellulose
Sample No.	1	2	3	4	5	6	7
Colour	Clear colorless	Brown	White	Yellow	Black	Brown	Black
Analysis, per cent.:							
Cellulose acetate, dry basis	97.3	91.5	82.7	78.0	95.0	78.5	70.0
Wood flour, dry basis	Nil	Nil	Nil	Nil	Nil	15.0	Nil
Moisture	2.7	4.0	2.8	4.5	4.5	4.5	1.0
Mineral pigment or filler	—	4.5	14.5	17.5	0.5	2.0	29.0
	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Nature of Colorant	Nil	Spirit soluble dye	Mineral	Aluminium lake	Aluminium lake	Aluminium lake and mineral pigment	Aluminium lake
Nature of mineral pigment or filler	Nil	Oxides of iron and manganese	Oxides of aluminium and zinc	Aluminium oxide	Nil	Iron oxide	Aluminium oxide
Particle size, per cent.:							
Retained on 20 mesh	20	85	86	80	85	90	66
Passing 20, retained on 40 mesh	40	10	12	15	12	7	15
Passing 40, retained on 60 mesh	36	3	2	5	2	3	7
Passing 60 mesh	4	2	0	0	1	0	12

importance, and the raw material must be free from bark and from any accidental contamination such as earthy matter. The wood flour retains the structural characteristics of the wood fibre. In other words, it is not made by one of the autoclave pressure/steam explosion methods, but by grinding processes originally developed in Sweden. It is believed that impact methods are also satisfactory for its preparation, e.g., the hammer-type suaging mill of the "Miracle" variety. Microscopically, wood flour should reveal its fibrous nature, reasonable uniformity in size and freedom from foreign matter, such as metallic inclusions and abrasive particles. A range of grades is available with respect to particle size, and 80 mesh is the average general purposes material. The average length of the individual wood fibres is from 0.002 to 0.007 in. It has a natural moisture content which fluctuates according to the humidity of exposure, a property common to all fibrous products. From 5 to 6 per cent. total water content (determined by loss in weight when heated at 105 degrees C. to constant weight) is usual, and 6 per cent. maximum a suitable value for specification purposes. This moisture aspect must be always borne in mind. When compounded with plastic, the moisture is largely sealed in, and if electrical properties are critical some trouble may arise. Consequently, for some purposes, it is essential to bake the wood flour at a controlled temperature in an indirectly heated oven to remove all traces of moisture before compounding, and then to mix with the plastic while still hot without any exposure delay during which moisture could be reabsorbed. Always it is advisable to keep containers of wood flour sealed to prevent excessive absorption under damp conditions. Likewise, when using wood-filled moulding powders, containers should be kept closed when not in use because the same tendency exists owing to the enormous surface area presented by the powder. For high electrical characteristics, the moulding powders are dried and kept warm for moulding.

The ready manner in which dry wood meal absorbs moisture and responds to humidity variations is

illustrated by the values given in Table No. 12. These data are demonstrated pictorially in Fig. 2.

Wood flour is almost universally employed in phenolic moulding compositions as a reinforcing agent. It aids flow of the composition during moulding in so far as it assists in equalizing stresses. It reduces shrinkage upon cooling, and aids stability by reducing moulding stresses to a minimum. It offsets the brittle nature of the cured resinous product and thus provides mechanical strength to resist impact and vibration. By proper choice of wood flour, percentage used, and mode of incorporation, perfectly sound stable mouldings result. For general purposes, these are resistant to temperature and humidity fluctuations as well as to exposure to continuous moderate heat, or to continuous water or oil immersion. Electrical properties are good but can be further improved upon by the baking treatment mentioned above. For maximum immunity under these conditions, special fillers are employed, as noted in later sections of this article.

Fig. 3, taken from "Industrial Plastics," by H. R. Simonds, correlates compressive strength and specific gravity of phenolic mouldings with the percentage of wood flour they contain.

Table 12.—Re-absorption of Moisture by Dry Wood Flour—Typical Values for Various Humidities.

Per cent. water re-absorbed during exposure	Per cent. humidity at 20°C.		
	50%	75%	100%
½ hour	2.9	4.9	8.4
¼ hour	3.9	6.7	10.6
1 hour	4.0	8.5	12.2
2 hours	(Constant weight)	9.0	14.5
4 hours		9.6	16.1
7 hours		9.9	17.5
20 hours		(Constant weight)	20.6
24 hours			20.6 (Constant weight)

Closely similar to wood flour is nut meal, prepared from the shells of nuts. The moulding industry is a useful outlet for this raw material, although, of course, there is not the same assurance with respect to continuity of supply.

Wood meal is similarly a general purposes filler for the amino plastics.

Regarding the thermoplastic moulding powders, cellulose acetate, benzyl cellulose, methyl methacrylate and polystyrene, these are mostly employed clear, coloured or pigmented, but without filler. However, for some purposes, the usual fillers can be employed; wood meal is used, for example, in cellulose acetate to reduce shrinkage of the moulded article during cooling. It thus eliminates those surface cavities so charac-

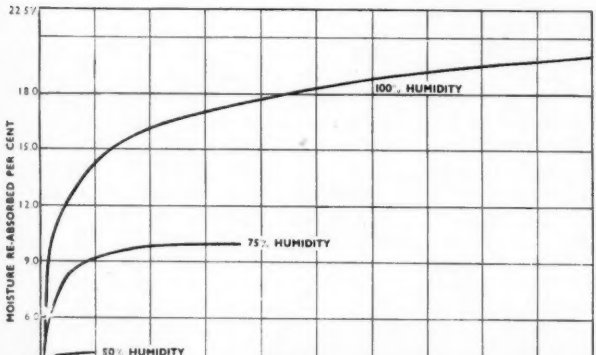


Fig. 2.—Re-absorption of water by dry wood flour at various humidities.

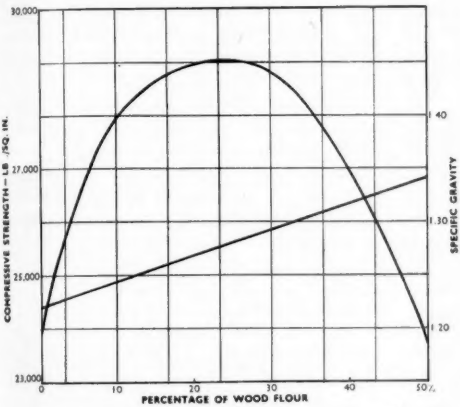


Fig. 3.—Influence of wood flour on compressive strength and specific gravity of phenolic mouldings.

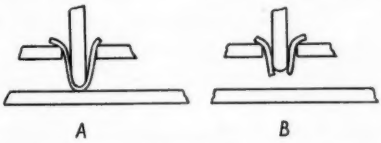


Fig. 4.—Softening points of thermoplastics.
A.—Pigmented or mineral-loaded.
B.—Wood flour filler.

teristic of acetate mouldings, or reduces them to a minimum. It also raises the apparent softening point of the moulding, thus rendering the thermoplastic materials serviceable at a slightly higher working temperature. The latter fact is clearly shown in Table No. 4, in which sample No. 6, with only 15 per cent. wood filler, exhibits a softening point 10 degrees C. higher than the average value of the other cellulose acetates illustrated. The table also shows that a similar percentage of mineral loading does not promote any appreciable rise in softening point (cf. samples Nos. 3 and 4 with sample No. 9). The wood constituent greatly reduces the ductility of the cellulose acetate moulding, and even the melting point test clearly shows this. Thus the acetates without wood filler show a clearly defined extruded cone in this test, whereas those containing wood rupture shortly after extrusion commences and then cease to move further. For clarity, this distinction is shown in Fig. 4.

Wood flour is also used as a filler for nitro cellulose cements or adhesives. In these it retards shrinkage during drying and "breaks" the continuity of film so that "ageing" shrinkage does not cause the film to pull away from the base material. Such cements are useful for plugging holes and for filling cracks and crevices, as well as adhesives for securing porous materials, such as earthenware, wood, fibrous compositions, etc. Indeed, these compositions, sometimes called "plastic wood," serve a useful function to the public.

Cotton and Silk for Moulding Powders

Cotton is used in the form of flock or linters; silk is similarly employed. These are not easy raw materials to handle because they tend to ball-up or cluster in small lumps. The latter must be parted before use and every care taken during blending to prevent

Table 13.—Re-absorption of Moisture by Dry Cotton—Typical Values for Various Humidities.

Per cent. water re-absorbed during exposure period of:	Per cent. humidity at 20°C.		
	50%	75%	100%
½ hour	3.0	5.2	7.6
½ hour	4.5	7.1	9.5
1 hour	4.9	9.0	11.0
2 hours	4.9	9.5	13.0
4 hours	(Constant weight)	10.0	14.5
7 hours		10.5	15.8
20 hours		10.5	18.0
24 hours		(Constant weight)	18.0 (Constant weight)

further clotting. Like wood meal, these textiles are hygroscopic and the same precautions must be taken. Table No. 13 gives numerical data which record the rate of moisture reabsorption by typical samples of cotton, while Fig. 5 depicts these graphically. Uniform dispersion of the textile throughout the moulding powder must be secured if full advantage of the shock-resistance qualities it imparts is to be secured.

Chopped cotton and silk fabric are used as alternatives to the fibres, largely with the elimination of the clustering problem. Again, fabric previously impregnated with plastic through the agency of varnish is also used, and this completely removes the difficulty. On the other hand, it is considered that the same degree of impact resistance is not quite achieved.

Choice of one or other of the above alternatives is largely determined by the requirements of the particular moulding. If thin sections are involved, or if much surface machining is subsequently to be performed, silk is the best material to use. Cotton flock is the next alternative, and chopped cambric for the coarsest purposes.

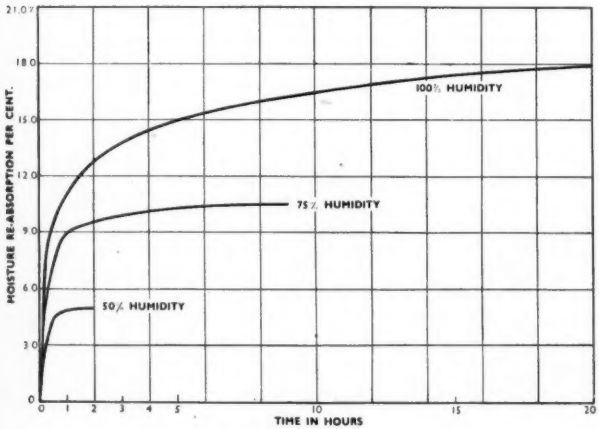


Fig. 5.—Moisture re-absorption by dry cotton at various humidities.

The object of using textile filler is to improve shock resistance beyond that obtainable from the best wood flour filled mouldings. Provided uniformity of distribution is achieved—and this applies not merely to the moulding powder but also to the moulded product—expectations are fulfilled. However, design of moulding, and of moulding tool, must be correct for the particular powder selected. Otherwise irregularity occurs in the moulding due to a tendency for the flock to filter out in the more constricted portions of the tool.

Paper in Moulding Powders

Paper in sheet form as filler for laminated boards, tubes and rods is common for the phenolic and amino plastics, but it also plays its part in moulding powders. Chopped paper is used in phenolics to provide greater impact strength than is obtained by using wood meal, although it has no obvious advantages over cotton fillers. It is claimed, however, that, with specific configurations of mouldings, greater impact strength is acquired, while also the compactness of the finished product permits of drilling and tapping with cleaner holes resulting. As with wood meal and textiles, paper is a hygroscopic material which breathes and responds to the fluctuations of the humidity of the atmosphere to which exposed. This is revealed by the test figures given in Table No. 4 and graphed in Fig. 6. These show

the absorption of moisture by dried paper until equilibrium is obtained in atmospheres of different hygrometric states.

In the case of the amino plastics, much paper filler is employed in preference to wood meal. It is used in the form of pulp or alpha-cellulose sheet, and is impregnated with the amino resin in aqueous syrup form. The process is operated hot, the syrup being introduced under vacuum and forced to penetrate the filler by applying a pressure of 5 to 10 atmospheres. The dried material is ground and pigments subsequently incorporated. The preference for cellulose in the form of cotton or paper for the aminos, rather than using the cheaper and rather less-pure wood meal, is accounted for by the fact that in some obscure manner combination between urea resins and cellulose occurs. As a result, the product is translucent, and wherever this property is required paper filling is advantageous. In this respect, the sharp contrast with phenolics is to be noted. The translucency is promoted by the vacuum-pressure impregnation process, which warrants full control attention to this end. Selected mineral fillers in small percentage may be present during the impregnation process to improve the mixture as a basis for pale shades of moulding powders. The white pigments, such as lithopone or titanium oxide, can be so used in small percentages. For highly filled moulding powders, the cellulose-urea resin mixture can be mechanically mixed with further cellulose, either wood meal or paper, to yield moulding powders with up to 85 per cent. cellulose filling.

The cellulose filling in amino plastics greatly improves their stability and resistance to weathering.

For phenolics, paper can be employed in the chopped dry condition and incorporated in the moulding paper by the solvent process. As, however, relatively large pieces of paper may be in the mix, a more convenient mode of introduction is in the form of paper coated or impregnated with a phenolic resin varnish. The paper base for such phenolized papers is generally a chemical wood stock paper, derived from clean stock and of long fibre. It should be closely neutral in reaction, that is, as free from residual chemicals as good commercial practice permits. From this angle, the pH value of the paper should be within the limits of 6.5 min.-8.5 max. It should be free from sizing and mineral loading, and the ash on incineration should be that due to the fibre alone, not exceeding 1.5 per cent. Various thicknesses can be used according to the requirements of the

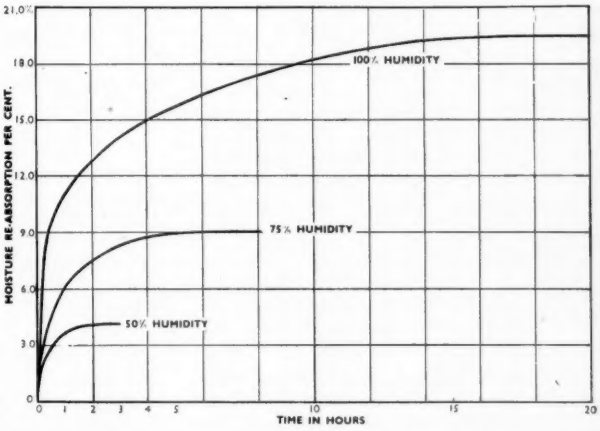


Fig. 6.—Moisture re-absorption by dry paper at various humidities.

Table 14.—Re-absorption of Moisture by Dry Paper—Typical Values for Various Humidities.

Per cent. water re-absorbed during exposure period of:	Per cent. humidity at 20°C.		
	50%	75%	100%
½ hour	2.2	3.1	7.7
½ hour	3.1	4.5	9.5
1 hour	3.8	6.2	11.1
2 hours	4.0	7.5	12.8
4 hours	Constant weight	8.9	15.0
7 hours		9.0	17.0
20 hours		Constant weight	19.5
24 hours			19.5
			Constant weight

ultimate moulding powder, and 0.002 in. to 0.005 in. is a typical range. The degree of varnishing can vary over a wide range, but sound limits for resin content within which to work are 40 per cent. min., 60 per cent. max., expressed in terms of per cent. by weight of the varnished paper. Table No. 15 depicts some typical commercial Bakelized papers.

Apart from these relatively heavy substance papers, which fall within the category commercially known as "Kraft," thinner-gauge papers down to 0.0003 in./0.0005 in. of chemical wood or rag stock can similarly be employed, and would be, in fact, essential for moulding powders destined for delicate configurations or for those having thin sections or webs.

Asbestos Powder

Asbestos is employed as a filler of the fibrous class because of its non-ignitable qualities. It can give mouldings that will withstand higher temperatures without carbonization than will the other fibrous materials, such as wood flour, cotton or silk. On the other hand, it does not impart the same degree of mechanical strength as these latter materials, and, consequently, is often employed together with one of them. It is used with phenolic and with cold moulding compositions.

One of the grades of powder like asbestos, commercially designated micro-asbestos or floats, can be chosen. For moulded products of good appearance, short-fibre material has to be employed with sacrifice of some mechanical strength. When appearance is not required to be of first order, longer-fibre asbestos is always used.

From the viewpoint of the producer of moulding powders, asbestos has two disadvantages that must be taken care of in the technique of mixing with the

Table 15.—Characteristics of Phenolized Papers.

Sample No.	Colour	Overall thickness, inches			Resin Content %	Ash %	Substance grams/sq. metre	Thickness, paper base, inches		
		Max.	Min.	Mean				Max.	Min.	Mean
1	Natural	0.0066	0.0061	0.0066	38.0	0.74	156.0	0.0057	0.0047	0.0052
2	Natural	0.0028	0.0024	0.0026	42.8	0.47	61.3	0.0020	0.0015	0.0018
3	Natural	0.0032	0.0027	0.0030	31.5	0.56	68.5	0.0023	0.0017	0.0020
4	Natural	0.0045	0.0040	0.0042	43.5	0.52	81.5	0.0036	0.0026	0.0031
5	Natural	0.0080	0.0068	0.0075	44.3	0.48	157.5	0.0055	0.0050	0.0053
6	Natural	0.0095	0.0086	0.0091	47.6	0.51	187.3	0.0085	0.0076	0.0075
7	Natural	0.0041	0.0034	0.0037	47.2	0.43	88.7	0.0030	0.0025	0.0027
8	Black	0.0089	0.0059	0.0077	48.5	0.59	160.5	0.0060	0.0052	0.0055
9	Black	0.0101	0.0090	0.0095	47.6	0.46	185.3	0.0089	0.0077	0.0078

All samples chemical wood stock base, clean, long fibres. All samples entirely neutral in reaction.

plastic. It is non-absorbent and it is fragile and easily pulverized. In these two respects it contrasts with the other fibrous fillers. The first renders it essential for a good moulding powder to work by the wet process. The plastic in varnish form is mixed with the filler, taking care to coat every particle. Solvent is then removed by heat or vacuum, or both, according to the nature of the plastic. The second factor renders precautions necessary with the grinding of the moulding material to avoid destruction of the fibrous character. Grinding times must be minimized and machinery chosen to have the least pulverizing effect. The suaging types of mills seem most appropriate for the purpose.

For moulding powders destined for electrical purposes, attention should be given to the compositional purity of the asbestos. Chemically, the most inert asbestos is a calcium magnesium meta silicate, $CaMg_3(SiO_3)_4$, but it is liable to contain other ingredients, such as magnesia, iron oxide, earthy material, and even metallic inclusions such as iron. Their absence should be ensured, and it is good practice to sieve out anything finer than 20 mesh in order to remove foreign contamination.

There are several other groups of "asbestos" dependent upon their natural origin; they vary in composition. Similar to the calcium magnesium silicate ("horneblende" or "amphibole") is a number in which iron or sodium chemically replaces a portion or all of the calcium or magnesium. These grades are not so inert and not so acid resisting.

Table 16.—Summary of Data upon Asbestos.

Average characteristics	Mineral group	
	Amphibole	Serpentine
General colour of fibre	Blueish lavender	White
Nature of fibre ..	Springy, harsh	Soft and silky
Specific gravity, average	3.25	2.25
Strength, tension ..	Poor	Good
Strength, flexing ..	Poor	Good
Solubility in acid, average (hydrochloric) ..	10%	60%
Critical temperature..	300°C.	400°C.
Iron content	0 to 35%	Very low

Laboratory Characteristics on Serpentine Asbestos, Commercial Fibres.

	Sample 1	Sample 2
Moisture content, loss at 110°C.	0.36%	0.31%
Loss on ignition, combined water	9.8%	10.1%
Asbestos, magnesium silicate base	89.8%	89.6%
Fibre size	$\frac{1}{8}$" to $\frac{1}{4}$"	$\frac{1}{8}$" to $\frac{1}{4}$"

Again, there are the "serpentine" asbestoses of approximate composition $H_4Mg_3Si_2O_9$, which, in effect, contain combined moisture, which tends to become liberated at about 300 degrees C., or during prolonged heating at lower temperatures. On the other hand, they are softer in texture and lower in density (2.25 against 3.25 for the horneblende asbestos). However, the advantages of the horneblende group outweigh these features. Some further information upon asbestos is given in Table No. 16.

(To be continued)

Stockport Plastics Exhibition

The Stockport (near Manchester) museum authorities are collecting material for an exhibition which they propose to hold in the near future, which will depict many phases of the plastic industry.

Previous industrial exhibitions have attracted visitors at the rate of 2,000 a day and it is expected that greater interest will be shown in this proposed Plastics exhibition, it being such a topical subject.

It is hoped that a representative exhibit of the whole industry will be collected and large manufacturing concerns are being approached in spite of the obvious difficulties in time of war. The objects shown will necessarily exclude plastics directly concerned with war production.

PRODUCTION NEWS

Raw Materials, New Plant, Works Organization, Control Apparatus, Research, Personal and Trade Notes

EXPORT OF GOODS. — Under the Export of Goods (Control) (No. 34) Order, 1942, (S.R. and O. 1942, No. 1640, price 1d.) which came into force on September 7, 1942, control is extended to cover additional metal manufactures, machinery, electrical goods (including wireless apparatus) and chemicals; spectacles and sunglasses made from plastic material; cork stoppers; unexposed sensitized photographic film.

I.—Licences will, in future, be required to export the following classes of goods to all destinations. (We include only those that may affect the plastics industry.)

Spectacles (including sunglasses) with frames, sides or rims wholly or partly of plastic material; and parts thereof wholly or partly of plastic material.

Articles of the following descriptions made wholly or mainly of non-precious metal:—

Boxes, jewel and trinket.
Spectacle cases.
Amplifiers of the thermionic valve-incorporating type.

Gramophones, radio gramophones and record players and parts therefor, the following:—

Gramophones, radio gramophones and record players.
Pick-ups.
Units incorporating electric motors.

Headphones and earpieces and headbands therefor.
Hearing aid appliances designed for the use of the deaf.
Loudspeakers and loudspeaker units.
Microphones.
Wireless receiving sets and receiver chassis.
Wireless transmitting apparatus.
Ethyl cellulose (cellulose ethyl ether) and preparations thereof.
Unexposed sensitized photographic film (other than paper film).

II.—Existing controls have been extended to cover hand and bench tools (and parts thereof) made wholly or mainly of metal and all kinds of containers (including flattened containers) and hollow ware.

III.—The existing licensing requirements with respect to caps, capsules and sprinkler tops wholly or mainly of metal; musical instruments; bristles of the pig, hog or boar; wireless valves.

EAST AFRICAN IMPORT RESTRICTIONS.—Colonial Governments in East Africa (Kenya, Uganda, Tanganyika and Zanzibar) have announced that further restrictions on imports from overseas are to be imposed and imports are to be graded in three priority ratings in order that shipping space may be used to the best advantage. All existing licences to import goods from the United Kingdom have been recalled for review and a large number of them will have to be cancelled. Importation of United Kingdom goods covered by cancelled licences will be allowed provided that the shipment from the United Kingdom was effected before August 31, 1942. Import licences (including re-issues of recalled licences) will in future be in a new form, indicating the priority rating, and will be issued in duplicate so that one copy may be sent to the overseas supplier. Instead of duplicate licences, airgraph certificates will, if desired, be issued to the importers for transmission to suppliers.

SCARCITY OF SHELLAC.—The lack of imported shellac into this country has started a campaign for the collection of 10,000,000 gramophone records for remelting and recovery. The campaign has been opened by the British Legion and over 6,000 depot secretaries are engaged in the collection and transport of discarded old records. Ten-in. or 12-in. discs of the following types are urgently required:—H.M.V., Columbia, Parlophone, Regal Zonophone, Zonophone, Brunswick, Decca, Rex and Panachord. Records should be handed in or sent to local British Legion depots, the addresses of which may be obtained at local post offices.

SYNTHETIC RUBBER.—The names of the Synthetic Rubber Committee have been announced in the House of Commons. They are:—

Chairman: Mr. F. W. Bain, chairman of the Chemical Control Board of the Ministry of Supply

Members: Sir Edward V. Appleton,

K.C.B., D.Sc., LL.D., F.R.S., of the Department of Scientific and Industrial Research; Dr. J. W. Armit, B.Sc., Ph.D., director-general of explosives at the Ministry of Supply; Sir Robert Robinson, D.Sc., LL.D., F.R.S., Waynflete professor of chemistry at Oxford; Dr. F. Roffey, B.Sc., Ph.D., A.I.C., controller of chemical research at the Ministry of Supply.

Sir Andrew Duncan, in reply to a question, said that the committee was to investigate possible methods of manufacture of synthetic rubber, not to organize the manufacture of the commodity.

SOUTH BEND LATHE.—A new bench model turret lathe for rapid production to close tolerances on chucking operations or bar work has just been announced by the South Bend Lathe Works. This lathe has a 10-in. swing over the bed and saddle wings, $1\frac{3}{8}$-in. hole through the headstock spindle, and 1-in. collet capacity. It is well adapted for second operation work.

The handlever operated bed turret indexes automatically, and has an adjustable stop for each of the six turret faces. The lathe is equipped with both a compound rest cross slide and a handlever cross slide, which are interchangeable. The latter is furnished with front and rear tool blocks which provide three tool positions. A quick-change gearbox supplies 48 longitudinal power feeds for the universal carriage, 48 power cross feeds for the compound rest cross slide, and 48 thread-cutting feeds, 4 to 224 per inch. The underneath motor drive and back gears deliver twelve spindle speeds.

A large assortment of attachments and accessories simplify tooling for specialized work or second operation jobs. For information, write to South Bend Lathe Works, Department 1P, South Bend, Indiana.

FIRE PROTECTION AND A.R.P. YEAR BOOK.—This annual handbook, first published in 1939, has now firmly established itself as the reference book for all those connected with fire-fighting and civil defence. This reputation has largely been attained by the reliability of the information to be found within its pages, the whole of the material being revised and brought up to date for each new edition. No mean task is thus involved as a result of the changes constantly being wrought in the organization, personnel, training and equipment of the Civil Defence (General) Services, and latterly by the formation of the National Fire Service.

The principal feature of the 1942-43 edition is an entirely new section, illustrated with especially drawn maps of each Region showing Fire Force Area boundaries, devoted to appointments in the National Fire Service. Published by Lomax Erskine and Co., Ltd., Aldwych House, London, W.C.2. Price 7s. 6d. post free.

CELANESE PLASTICS DEVELOPMENT, LTD.—Following the announcement of the registration of this company, given in our August issue, British Celanese, Ltd., have issued further details regarding the new concern.

The initial capital of Celanese Plastics Development, Ltd., is £300,000. The Board is as follows:

Sir John Wardlaw-Milne, K.B.E., M.P., chairman.
Sir Harold Webbe, M.P.
Mr. J. H. Rooney.
Dr. G. Rudorf.
Dr. N. A. C. Friend.

The latter three directors have been connected with British Celanese in its commercial, technical and scientific activities for a long time.

The registered office of the company is at Celanese House, 22-23, Hanover Square, W.1. and the secretary is Mr. A. R. Currie, who has been assistant secretary to British Celanese, Ltd., for many years.

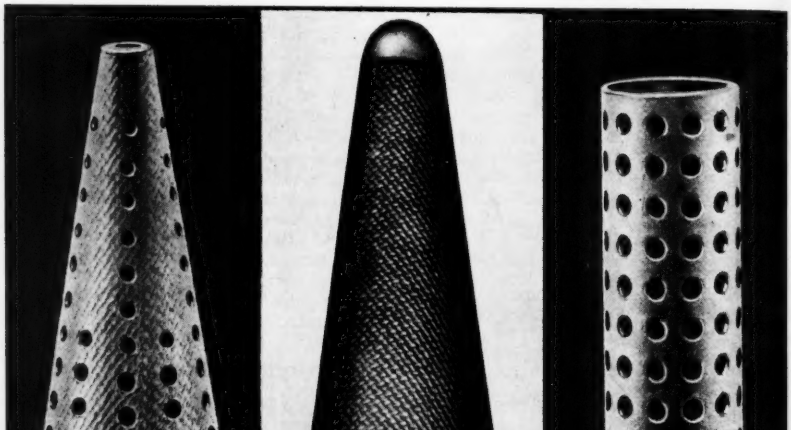
LACRINOID, LTD.—Mr. H. R. Thurlow Prior, Mr. A. H. Johnson, O.B.E., and Mr. A. van Beugen Bik, have resigned from the Board of Directors and Mr. T. L. Horabin, M.P., and Sir Louis Sterling have been elected chairman and deputy chairman respectively. Mr. A. Bernstein, the original founder of the business, will continue as managing director.

BRITISH ARTID PLASTICS, LTD.—Mr. C. H. Appleby, F.C.A., has recently been elected to the Board of this company.

Personal

ERIC REAVELL.—We regret to announce the death of Mr. Eric Reavell at the early age of 42. He was a director of Kestner Evaporator and Engineering Co., the well-known chemical engineering concern that has made such remarkable progress in the production of chemical plant made from Haveg, the asbestos-filled phenolic resin. He was a scientist of high order and interested himself very early in the plastics industry.

TUBES—by the MILLION



Some Notes on the Modern Production of Resin Impregnated Paper Tubes for the Textile and Other Industries at the Works of the Textile Paper Tube Co., Ltd.

OF the industries employing non-metallic tubes in processing or manufacture, there is no doubt that the textile industry is the largest user. Indeed, this is not surprising since the textile industry is itself so great and since, also, from the initial yarn spinning through the various chemical treatments to the final weaving or knitting of fabric or garments, cotton, wool, silk, jute, hemp and other fibres are wound on tubes. Tubes of various qualities, to withstand boiling water and steam treatment, the action of alkalis and other corrosive liquors, dyeing and other processes, or tubes that are merely structures to support the fibre and do not come into contact with liquids are made in hundreds of millions. Of these by far the largest number are of paper.

A recent visit to the works of the Textile Paper Tube Co., Ltd., of Romiley, near Stockport, has given us a view of this great paper tube-making industry, and, what is more important, an insight into one of the most modern plants in this country. An interesting feature is the manner in which plastics has been adopted for the introduction of special

improvements to withstand high temperature and the action of chemicals.

Briefly, there are two main classes of paper tubes:—

1. Untreated paper tube; this is one made from a high-class paper by the use of adhesives such as flour, starch, casein, etc. This type of tube is used where there is no special processing of the yarns whilst on the tube.

2. Resin-treated paper tubes. During recent years there has been a big demand for paper tubes carrying fibres to withstand hot dye liquors, washing processes, caustic soda treatment, etc. Some 10 years ago the Textile Paper Tube Co., Ltd., installed a large resin impregnated plant for the treatment of tubes using thermo-hardening resins of the phenol-formaldehyde type as impregnating medium. The process is patented, this company holding the sole British rights.

While also such treated tubes are generally called "bakelized" paper tubes, there is a considerable difference between those produced at this factory and those commonly made for specialized electrical work. The normal process adopted for the latter work has often been described in these pages and is a comparatively small capacity, slow type of work, since the paper is coated with resin and then wound on heated mandrels.

The Textile Paper Tube Co.'s process, on the other hand, differs from the preceding one in that untreated tubes are produced on automatic machinery and are then impregnated. Since the automatic machinery is extremely fast, the rate of production is enormous. It will be seen, therefore, that the process is admirably suitable for the production of large quantities.

The types of tubes made are not merely straight tubes. The tapered form, in fact, any tubular or conical shape is a potential product. Furthermore, in order to meet requirements for a variety of purposes, the resin content can be controlled as desired. This range covers a demand for tubes used in processes employing a variety of chemicals or temperatures, or, alternatively, a demand for tubes of different strengths, flexibility and freedom from chipping.

During the past few years, the demand for paper tubes to replace metal, glass, wood and other structures has rapidly increased. The inherent value in a strong paper tube which is corrosion-resisting is now being fully realized in industries that have hitherto been thinking only in terms of metal.

PRESSES FOR PLASTICS

(Continued from p. 299)

needs no more than periodic attention.

The trend of development is to have central pressure-water plants arranged outside the actual shop. Pressure accumulators are subdivided into low-pressure units up to 225 lb./sq. in. (quick approach), medium-pressure units, 900-2,240 lb./sq. in. (for pre-pressing or mould removal), and high-pressure accumulators from 2,800-4,500 lb./sq. in. for the moulding operation.

The modern accumulator is invariably operated to-day by compressed air supplied by a high-pressure compressor. Control is fully automatic, either hydro-pneumatic or electro-hydraulic, the last-mentioned method having the advantage that, in operation, it is practically free from change due to friction variation.

Safety devices are provided to guard against over pressure and excessive consumption of pressure water. This last point must be attended to, as, if the accumulator become exhausted of water, high-pressure air passes direct into the press.

The apparent disadvantage of an accumulator service with only a single high-pressure stage and, therefore, only a single useful pressure to all presses, can be balanced by the provision of pressure-reducing apparatus or valves.

Resinoids and Other Plastics as Film Formers

By B. J. BRAJNIKOFF,
Consulting Electrical Engineer

XI.—Structural Aspects of Styrene Polymers

AMONG the numerous possible ways of synthesizing the rubber-like plastics, sometimes termed elastomers or elastoprenes, of prime importance to the coating industry, the chief place belongs to the butadienoid compounds. Butadiene may be readily produced either from acetylene, or by cracking of petroleum.[132] As estimated by Egloff,[133] it can be manufactured in enormous quantities at a price which is bound to promote its utilization on an extensive scale. It is also well to note that there recently emerged a new source of butadiene, peculiar to Germany, viz., from that type of installation which may be classed as the "carbide-alcohol" plant. This yields ethyl alcohol by using calcium carbide as raw material.

Butadiene, $CH_2 = CH - CH = CH_2$, is a highly mobile colourless liquid with a faint odour, boiling at −4 degrees C.; the vapour pressure of butadiene at room temperature is about 3 atmospheres. In contradistinction to ethylene, which is stable and polymerizable only under the influence of high pressures or powerful catalysts, yielding rather moderate weight polymers, butadiene polymerizes readily, giving rubber-like products of high molecular weight; here, the conjugation of the double bond of ethylene with another ethylenic bond is displayed even stronger than the conjugation of the double bond of the side chain of styrene with the double bonds of benzene nucleus. Thus, according to Fawcett,[134] the polymerization of ethylene under ordinary or slightly elevated pressure, with or without catalysts, results in the formation of liquid products with molecular weight from 100 to 500; only at 170 degrees C. and under the pressure of 1,000 atmospheres, the reaction yields a solid polymer having molecular weight about 4,000.

Special Polymerization Methods

The slow conversion of divinyl, its homologues and other hydrocarbon substitution derivatives thereof by self-polymerization into rubber-like plastics can be accelerated by chemical and physical means; but its speed is enormously increased, as it has been demonstrated by Ostromislensky,[135] by photo-chemical action, e.g., ultra-violet rays. Ostromislensky used in the photo-polymerization the ultra-violet radiations of a mercury arc lamp, rated at 110 volts, 2.5 amperes; by increasing the strength of the current, but keeping the electric pressure unaltered, the chemical action of the rays is considerably intensified, with the result that the reaction is accelerated. The polymerization process can be accomplished at normal, or even at a lowered temperature by placing the monomeric substance, in a free state or in solution or emulsion, into a suitable vessel, which is exposed to the influence of the active radiations. Cathode rays, Röntgen rays, silent electrical discharges, or combination of rotating electro-magnetic field applied to a stream of cathode rays act in the same way, resulting in accelerating the chemical reactions by spirally moving electrons, whose effect is increasing in proportion to the raising frequency of the field.

Importance of Butadienoid Systems

The known fact that the incorporation of an aromatic nucleus into the divinyl molecule leads to a great improvement in the properties of the resultant product, may be turned to special account by combining butadiene and styrene in a man-

ner so as to secure co-polymers with features designed to meet new applications. The following development illustrates the point.

The rapid strides in the electrical technology makes it now possible to add to the two basic forms of the electric energy transmission—through conductors and by wireless—a third new form,[136] which, although at present is of scientific interest only, none the less will find its practical utility as the research on the decimetre and centimetre range of radio waves advances.

The problem connected with the aforesaid phenomena is analogous to wireless energy transmission, with the sole difference that the propagated waves are not radiated into space, but compelled to travel within a dielectric medium of a cylindrical shape, for example, in a metallic tubing filled with some insulating substance. With a correct selection of a wavelength and of the diameter of cylindrical dielectric, it is possible to replace entirely the metal envelope by insulating media enclosing this "dielectric conductor," for instance, by air, whereby the energy will not be dissipated into adjacent region but is canalized along the cylinder-shaped dielectric. There will be a complete reflection of electric waves at the boundary between both dielectric media, which will thus prevent their irradiation into surrounding space.

It is of interest to note that the possibility of such a development of transmitting energy over a cylindrically shaped dielectric had been predicted a few years ago on the basis of mathematical analysis, and the experiments performed in the U.S.A. in 1938 have confirmed this theory.[137] The future of this new extremely interesting form of electric energy transfer, over a single dielectric, dispensing with current-conducting metals, depends obviously on the degree of co-ordination between the results of further studies of such systems and the research on insulation.

Polystyrene, with its unique dielectric properties, viz., vanishingly small tan δ at 10^6 cycles = 0.0002, high volume resistivity $> 10^{18}$ ohms at the same frequency, immunity to moisture, etc., stands unrivalled in application to high-tension electric systems, where it competes with and can justifiably replace such high-grade and costly insulants as amber, shellac or mica.

Here is, therefore, a splendid opportunity for the plastics technologist to associate himself with the development, which is bound to provide not merely a new outlet for resinoids, but, what is even more important, to contribute a monumental share in the universal advancement of culture.

Since the service behaviour of plastics, including the performance of films derived from them, is governed, fundamentally, by the physical structure of their macro-molecules, it is important at this juncture to approach their molecular architecture more closely.

The Structure of Co-polymers of Styrol and Butadiene

The technical literature is profuse with indications as to methods that can be applied to the cross-polymerization with a view to obtaining new types of rubber-like synthetics.[138] There are, however, relatively few experimental data which would permit the forming of a definite notion on the structure of macro-molecular complexes derived as a result of such polyreactions.

Throughout the previous section, a special consideration has been given to the discussion of the cross-polymers of styrene and their ascendency in the film-forming field, particularly in the manufacture of the latex-like systems, which display properties in some respects superior to natural products.

The problem of ascertaining the structural aspects of plastic materials has lately received considerable attention. Although steps in this direction have been rapid, much in the way of further exploration is still to be done, especially in the realm of hybrid-resinoids. In this respect very notable has been the contribution of Dr. Alekseeva,[139] whose work, conducted at the Laboratory of Poly-

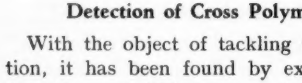
merization Processes, of the Moscow Institute of Physical Chemistry, materially helped to elucidate the structure of macromolecules derivable from cross-polymerizing styrene and butadiene.

During the cross-polymerization of vinyl benzene with divinyl, just as in other co-polymerizing reactions, it is possible to expect either the formation of a cross-polymer composed of a macromolecular mixture, made by the mutual association of the structural units of identical constitution, or the product of the cross-polymerization may be the co-polymer, whose macromolecules are built up by combining the structural units in an orderly pattern obeying some alternate regularity.

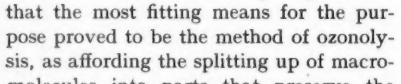
Detection of Cross Polymers

With the object of tackling this question, it has been found by experiments that the most fitting means for the purpose proved to be the method of ozonolysis, as affording the splitting up of macromolecules into parts that preserve the structure of the carbon skeleton of the substance formed. Subsequently, the decomposition products of ozonides were oxidized by diluted peroxide of hydrogen, and the resulting mixture of the acids was separated by means of their methyl ethers.

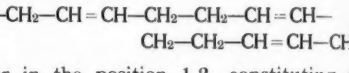
In the event of polymerizing each of the components independently, as would be expected, styrene should form a hydrocarbon of high molecular weight with the saturated-carbon chain and phenyl groups as the branch-chains.



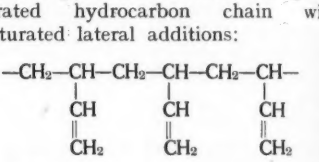
or



Such a hydrocarbon should be very stable in relation to ozone of low percentage. As regards butadiene, its molecules may unite in the position 1.4, forming high molecular unsaturated hydrocarbon with a normal chain:



or in the position 1.2, constituting the saturated hydrocarbon chain with unsaturated lateral additions:



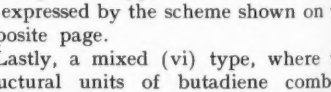
and, finally, in a single macromolecule can be combined both methods of association, which leads to the production of highly branched complexes. In the first case, as a result of ozonolysis, it is legitimate to expect the formation of the amber acid, in the second—the formic and high molecular polycarbonic acids, and in the third case—polycarbonic acid of fairly high molecular weight.

If, on the other hand, to assume that during the polymerization process a true cross-polymer was formed, then the structure of its macromolecules may be different, depending both upon the character of alternation and the manner of combining of the individual structural units.

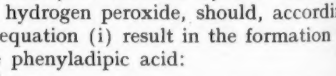
The possible types of combinations can be expressed by the scheme shown on the opposite page.

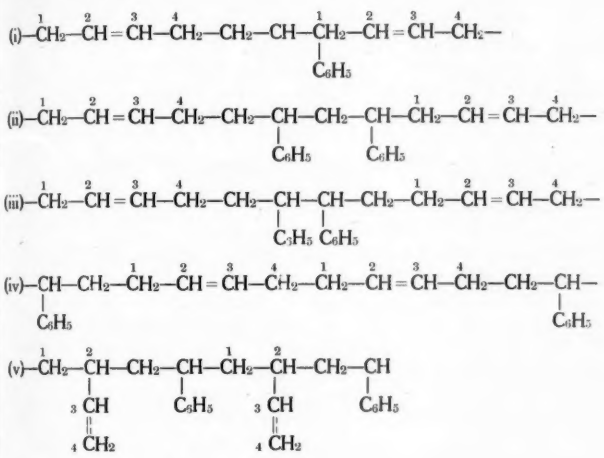
Lastly, a mixed (vi) type, where the structural units of butadiene combine with styrene molecules either in the position 1.2. or in the position 1.4. Such a mode of combination leads to the productions of branched macromolecules.

Ozonolysis, followed by the oxidation by hydrogen peroxide, should, according to equation (i) result in the formation of the phenyladipic acid:



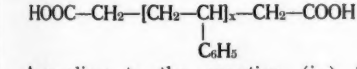
and on the basis of equations (ii) and (iii) should yield isomers of diphenyl-cork-wood acid:





Scheme showing possible types of cross polymers referred to on the previous page.

On the assumption that macromolecule is built up not by the two, but by a greater number of styrene molecules uniting with butadiene, it must follow that the derived acids conform to the type:—



According to the equation (iv) the resultant acids should be identical with those obtained in the preceding cases, and, in addition, also the amber acid, and the reactions (v) and (vi) must give the formic and high molecular polycarbonic acids.

Actually, there have been separated out and identified amber, formic, phenyladipic and diphenyl-corkwood acids. In addition, there were produced several high molecular acids of indeterminate structure, rich in carbon content, but with a small equivalent, which indicates that they were formed as a result of a mixture, in which butadiene molecules unite both in the position 1.2. as well as in the position 1.4.

Experimental Part

The production of co-polymers was effected by polymerizing styrene and butadiene together in proportion of 1:1 by weight, which in molecular respect corresponds to the ratio of one styrene molecule to two molecules of butadiene. Benzoyl peroxide served as the accelerating agent, which was introduced to the amount of 3 per cent. of the reaction mix. The polymerization process was conducted at 60 degrees C. for 210 hours. The polymeric product was then liberated from the admixture of monomers, first by the treatment at reduced pressure of 2 mm. Hg., after which it was comminuted and extracted with alcohol, with the subsequent removal of the latter in vacuo at 35 degrees to 40 degrees C. The polymer, free from monomers and alcohol, and carefully powdered, was then placed in small portions of about 1.5-2 grammes in 200 millilitres of dry chloroform, in which it was kept for three days; after this operation it was ozonized by the current of oxygen, containing 1.5 to 2 per cent. of ozone. The ozonizing treatment has been conducted with simultaneous cooling with ice until the complete solubility of the polymer was reached, which usually was attained within five to six hours from the start of the ozonizing stage. Chloroform was distilled off under a diminished pressure. The decomposition of ozonides was accomplished by the boiling with 3 per cent. solution of hydrogen peroxide. A part of the decomposition product passed into the aqueous solution, and another part was released

in the form of a light-yellowish wax-like mass soluble in alcohol. After decomposing the ozonide, the water solution was cooled and decanted from the insoluble sediment, which was thoroughly washed. The water used in this procedure was added to the aqueous solution. To remove the volatile products, the water solution was distilled in vacuo at about 30 degrees to 40 degrees C. The receiver was subjected to cooling with ice mixed with salt. The distillate has been examined with the object of determining the content of aldehydes and formic acid. The separation of the amber acid was effected by fractional crystallization of the non-volatile acids remaining after distilling off water. The residue was a light-yellow syrup-like mass.

The acids, both soluble and insoluble in water, were transformed into methyl ethers by means of dissolving them in absolute methyl alcohol containing 5 to 6 per cent. of dry hydrogen chloride. After keeping the solution in the cold for 24 hours, it was heated on the water bath with reflux condenser for 1½ hours, following which it has been treated in the usual manner. The mixtures of ethers resulting therefrom were separated out by vacuum distillation.

Results of Analysis

As a result of the foregoing treatment, 32 grammes of polymer yielded 3.22 grammes of formic acid (this was estimated by titration with alkali, which, for the purpose of control, was also checked by oxidation with the solution of potassium permanganate), 10.41 grammes of crystallized amber acid, 21.2 grammes of water-soluble acids, and 19 grammes of insoluble acids: 20 grammes of soluble acids gave 18.5 grammes of methyl ethers, by the vacuum distillation of which were produced the following fractions:—

Fraction 1, at 85 degrees C. and 2 mm. Hg., 4.2 grammes.

Fraction 2, at 125 degrees C. and 2 mm. Hg., 5.2 grammes.

Fraction 3, at 140 degrees C. and 0.05 mm. Hg., 2.8 grammes.

Fraction 4, at 170-180 degrees C. and 0.05 mm. Hg., 3.5 grammes.

Residue, 2.2 grammes.

Determination of Molecular Weights of Ethers by Cryoscopic Method

Fraction 2.—The amount of substance 0.1590 gramme : 21.1 grammes of CH_3COOH; Δ t 0.112 degree C.

The amount of substance 0.3207 gramme: 21.1 grammes of CH_3COOH; Δ t 0.233 degree C. Found: Molecular weight, 262-254.4; equivalent to $C_{14}H_{18}O_4$. Calculated: M.W.250.

Fraction 3.—The amount of substance 0.1700 gramme: 17.8 grammes of CH_3COOH; Δ t 0.152 degree C.

The amount of substance 0.2501 gramme: 17.8 grammes of CH_3COOH; Δ t 0.225 degree C.

Found: M.W. 245-240; $C_{13}H_{16}O_4$. Calculated M.W.235.

Fraction 4.—The amount of substance 0.2100 gramme: 24.1 grammes of CH_3COOH; Δ t 0.130 degree C.

The amount of substance 0.2901 gramme: 24.1 grammes of CH_3COOH; Δ t 0.177 degree C.

Found: M.W. 261.4-265.7; $C_{13}H_{16}O_5$. Calculated M 252.

Analysis of Ethers of Soluble Acids

Fraction 1.—The amount of substance 0.1574 gramme: 0.052 gramme of CO_2; 0.0959 gramme of H_2O. Found, per cent.: C 49.14; H 6.75 $C_6H_{10}O_4$. Calculated, per cent.: C 49.31; H 6.84.

Fraction 2.—The amount of substance 0.1887 gramme: 0.4647 gramme CO_2; 0.1180 gramme H_2O. Found, per cent.: C 67.51; H 6.95. $C_{17}H_{18}O_4$. Calculated, per cent.: C 67.20; H 7.25.

Fraction 3.—The amount of substance 0.1458 gramme: 0.3510 gramme CO_2; 0.0919 gramme H_2O. Found, per cent.: C 65.75; H 6.73. $C_{13}H_{16}O_4$. Calculated, per cent.: C 66.10; H 6.80.

Fraction 4.—The amount of substance 0.2001 gramme: 0.4569 gramme CO_2; 0.1143 gramme H_2O. Found, per cent.: C 62.25; H 6.71. $C_{13}H_{16}O_5$. Calculated, per cent.: C 61.90; H 6.34.

Residue.—The amount of substance

0.2204 gramme: 0.5472 gramme CO_2; 0.1369 gramme H_2O. Found, per cent.: C 67.72; H 6.90.

Nineteen grammes of insoluble acids gave 16.4 grammes of methyl ethers. gramme: 20.3 grammes CH_3COOH; Δ t 0.136 degree C. Found: M.W. 360-365. $C_{21}H_{24}O_4$. Calculated M.W.340.

The amount of substance 0.1887 gramme: 0.4800 gramme CO_2; 0.1180 gramme H_2O. Found, per cent.: C 69.38; H 6.95. $C_{21}H_{24}O_4$. Calculated, per cent.: C 74.11; H 7.06.

Table 1.—Determination of Equivalents of Ethers by Saponifying with Alkali.[139]

Fraction	Weight of substance in grammes	0.1 N. NaOH, in millilitres	0.1 N. HCl, in millilitres	Equivalent found	Equivalent calculated	Name of Ether
1	0.1460	50	30.09	73.32	73.	Dimethyl ether of amber acid
2	0.1564	37.13	24.41	123.	125.	Dimethyl ether of phenyladipic acid
3	0.1842	37.13	21.12	115.	118.	Monomethyl ether of phenyladipic acid
4	0.1830	37.13	22.13	122.	125.	Monomethyl ether of phenyloxyadipic acid
Residue	0.2260	46.03 0.5 N NaOH	42.02 0.5 N H_2SO_4	113.		

Table 2.[139]

Compound	Quantity of Substance in grammes	Butadiene in grammes	Styrol in grammes
Polymer	32.16	16.	16.
Formic acid	3.32	3.74	
Amber acid	10.41	4.76	
Dimethyl ether of amber acid	4.2	1.56	
Monomethyl ether of phenyladipic acid ..	2.8	0.64	1.24
Monomethyl ether of phenyloxyadipic acid ..	3.5	0.75	1.48
Monomethyl ether of diphenyl-corkwood acid	16.4	1.59	6.35

They could not be distilled off without decomposition even under extremely high vacuum.

Determination of Equivalents

The estimation of ether equivalents was effected by the saponification in the ether-alcohol-aqueous solution.

The amount of substance 33.72 millilitres 0.5 normal NaOH; 30.79 millilitres 0.5 normal H_2SO_4. Equivalent found 168.7; calculated 170.

The amount of substance 0.2100 gramme: 20.3 grammes CH_3COOH; Δ t 0,114 degree C.

The amount of substance 0.2550

The balance of styrol and butadiene content in the derived polymers and in the release products is given in Table 2.

Thus the number of the products obtained corresponds to 88.45 per cent. of butadiene and 71.1 per cent. of styrene calculated from that quantity which was contained in the initially produced polymer.

The formic acid has been derived as the result of a mixed type of combination of the structural units, where butadiene associated both in the position 1.2, as well as in the position 1.4, which ought to lead to the formation of branching molecules of relatively high molecular weight. The residue left after distilling off methyl ethers of soluble acids apparently belongs to this type of combinations, which so far have not been identified.

Conclusions

As may be seen from the above-presented data, the simultaneous polymerization of styrene and butadiene gives rise to the production of co-polymers of various composition.

Calculated from styrene, 31.2 per cent. of its monomer form with butadiene macromolecules, which display a regular

alternation of both structural units, where butadiene combines in the position 1.4.

Forty per cent. of styrene form macromolecules, which are built up by a successive combination of two styrene molecules; these pairs are separated by one or several molecules of butadiene, uniting in the position 1.4.

The remainder 29 per cent. of styrene, apparently, enters into the composition of the branching molecules, which are grown as a result of combining with butadiene, both in the position 1.2 and 1.4.

Taking into account that formic acid should be yielded by macromolecules, in which butadiene is combined in the position 1.2., it may be inferred that out of the entire butadiene polymer 23.3 per cent. of it polymerizes in the position 1.2, and the rest of butadiene in the position 1.2.

The Polymerizability of Substituted Styrenes in Relation to their Structure

Notwithstanding the fact that modern technology very frequently and on a large scale makes recourse to polymerization processes involving unsaturated hydrocarbons with the object of synthesizing rubber-like materials and other plastics, a great many theoretical questions of extreme importance arising in this field remain as yet obscure.

Side by side with a considerable progress achieved in elucidating the polymerization mechanics, due to the latest and extensive works of Staudinger and Carothers, and Katz and others by the Röntgenoscopic method for studying the constitution of derived polymers, systematic work on the connection between the chemical composition of monomers and their ability of polymerization is rare (with the only exception of dienes—substituted butadienes). Still less is known of the influence of isomerization of the fundamental molecules. No doubt, however, that, as a result of exploration of these problems, it may be possible to find certain regularities, the knowledge of which should be of great practical worth—they must provide the plastics technologist with the guiding path in the search for substances convertible by the polymerization into products with superior features. Up to now these efforts, as can be observed from the voluminous patent records, are being exerted in rather a crude empirical manner, by trial and error method. The first attempt in this direction has been by Professor Shorygin[140] in Russia, who selected for this investigation the substituted styrenes.

Interdependence Between the Structure of Monomeric Styrene and Chemistry of Coatings

The polymerization of simple styrene has been thoroughly studied in a number of works of Staudinger and his collaborators. In the course of polymerization the molecules of monomers combine with each other with the formation of more or less extended threadlike macromolecules, having possibly a double-chain structure due to cyclization.

At ordinary temperature the polymerization reaction progresses at an extremely slow rate (several months); on heating, the action proceeds rapidly (at 180 degrees C.—in a few hours). The polymerization at low temperatures yields polystyrene of the eucolloidal type with molecular weight of the order of 100,000-200,000, swellable in organic solvents, giving highly viscous solutions; by polymerizing styrol at high temperature level, polystyrenes of the hemicolloidal type are produced, which dissolve much more easily and without preliminary swelling, with molecular weight 3,500-10,000.

Staudinger and Breusch[141] have also examined the polymerization of alpha-methylstyrene (1-methyl-1-phenylethylene), $C_6H_5C(CH_3) = CH_2$, where it has been found that methyl group in α-position exerts a detrimental influence upon the polymerization: this derivative does not polymerize either on long standing or under the action of light, and consequently it cannot yield eucolloidal products. On heating and under the influence of catalysts, it polymerizes much more difficultly than a simple

Table 3.[140]

Hydrocarbon	Boiling point °C.	Specific gravity d_{24}^{24}	Refractive index n_D^{24}	Molecular refraction MR found	Molecular refraction MR calculated
Styrol	33–34 (at 7 mm. Hg.)	0.8923	1.5446	36.81	35.07
Ortho-methylstyrol	51 (at 9 mm. Hg.)	0.8912	1.5425	41.72	39.60
Meta-methylstyrol	52–53 (at 9 mm. Hg.)	0.9044	1.5400	40.94	39.60
Para-methylstyrol	51 (at 10 mm. Hg.)	0.8974	1.5395	41.22	39.60
Alpha-naphthylethylene ..	116–117 (at 8 mm. Hg.)	1.0439	1.6425	53.35	50.41

Table 4.[140]

Product of the Polymerization	η_{sp}. at 22° C.	GM	M.W	P	Temp. (°C.)	Characteristics of the Polymerizates.
Styrol	0.771	0.168	25,500	245	90–100	Hard, transparent, colourless vitreous mass.
Ortho-methylstyrol ..	0.881	0.136	35,990	274	120–130	As polymer of Styrol, but more elastic.
Meta-methylstyrol ..	0.800	0.136	32,680	255	105–110	As polystyrol, but harder and more brittle.
Para-methylstyrol ..	0.564	0.136	23,040	180	85– 95	As the preceding polymer, but brittler still.
Alpha-naphthylethylene ..	0.096	0.116	4,598	30	100–110	Transparent resinous mass, with the yellow-greenish tint, very brittle.

styrene, while giving hemicolloidal polymethylstyrols with the molecular weight 1,000-10,000, a circumstance, obviously, of the immediate and vital bearing on the chemistry of coatings.

In view of the foregoing harmful influence of the presence of the methyl group in the branch-chain of styrene, it has been decided to investigate its action in all three possible positions—ortho, meta and para. For this reason, first of all were prepared the corresponding alcohols (by means of the usual Grignard reaction), and from them were derived the isomeric methylstyrenes, through elimination of water (by heating with potassium hydroxide).

The physical properties of hydrocarbons prepared in this way for experiments, viz., styrol, ortho-methylstyrol, meta - methylstyrol, para - methylstyrol, and alpha-naphthylethylene, were of the high chemical purity, as may be judged from Table 3.

The polymerization of all these styrenes was carried out in identical conditions by simultaneous heating of all specimens, without catalytic agents, in sealed glass vessels, at 175 degrees C. for three hours.

The properties of the derived products are given in Table 4.

Their coefficient (or degree) of the polymerization, P, as well as their specific viscosity in 2 per cent. benzene solutions, η_{sp}, the molarity of the solutions (in 1 litre) calculated from the fundamental molecule, GM, molecular weight, M, were calculated by the known Staudinger's formula $\eta_{sp} = K_m \cdot C \cdot M$, where K_m is a constant for a given solvent, which for benzene solutions of styrene is equal to 1.8×10^{-4}; C denotes the concentration of polymers expressed in terms of the number of moles of the basic unit of polymer; the thermal stability, T, was evaluated (approximately) by the temperature of softening and fusion of polymerizates in capillary vessels.

The best mechanical properties (considerable elasticity) were shown by the polymeric ortho-methylstyrene. It was the only one that did not break on opening the test tubes, although it has been formed there in the shape of very thin layer and was taken out intact as a thin resilient plate.

For the sake of comparison of these products, which may be classed as hemi-

colloids, polymerized under perfectly similar conditions, it is possible to accept the degree of the polymerization as being the quotient from the division of the molecular weight (found by the specific viscosity method) by the molecular weight of the respective monomer. That the values so obtained possess certain real significance is confirmed by the fact that the physical properties of derived polymers vary parallel with the change of P; the most resilient, strong and stable to heat product of the polymerization was yielded by the ortho-methylstyrol, whose coefficient of the polymerization, P=274, surpassed all other polymeric bodies, and was appreciably higher than that of mechanically pure styrene; then followed, in turn, by the meta-isomer (P=255), pure polystyrol (P=245), para-isomer (P=180), with the last place allocated to a very brittle alpha-naphthylethylene (P=30), which, however, displayed a fair stability to heat, probably due to presence of the naphthalene nucleus. That polystyrenes thus obtained form the boundary zone between hemi- and eucolloids is indicated by the circumstance that, on heating their benzene solutions up to 60 degrees C., their specific viscosity is decreasing, and, on cooling, does not return to its original value.

Deductions

On the basis of the above-described experiments it is legitimate to deduce that the lengthening of the lateral groups in the fundamental valence chains of polystyrene (the greatest was that manifested by the para-methylstyrol) and a considerable increase in their weight (viz., the nucleus of naphthalene) reduces the capacity of styrene for the polymerization and worsens the properties of polymers produced under the same conditions (e.g., inferior thermal stability, lack of elasticity, brittleness, etc.); the only exception is the case of the methyl group in the ortho-position, which functions in the opposite sense.

In Staudinger's view, the negative influence due to increase in the length or weight of side-branches of polystyrene chains may be attributed to the inadequacy of mechanical strength and stability of very long, slender molecules in their over-growth.

If, on the other hand, to accept the validity of the micellar theory of Meyer's and Mark's, the lenthening and generally volumetric increase of the lateral branching should impede the association of the primary valence chains, owing to steric hindrances created by the branches.

Extension of Experiments

With the aim of verifying the correctness of the conclusions arrived at from the work as outlined above and to establish their validity and the scope on a broader experimental basis, the efforts of Shorygin's[142] school have been extended to a systematic study of the thermal polymerization of a number of other substituted styrenes, combining with them, for the purpose of comparison, certain other derivatives of ethylene that possess no aromatic nuclei.

Table 5 presents the physical constants of the monomers employed. Some of the compounds, namely, o- and p-bromstyrols, the primary diphenylethyl alcohol, the secondary o-bromphenyl alcohol, and secondary p-bromphenyl alcohol whose mode of production so far has not been described, were synthesized in the original manner; with regard to several others, the sole information was the figure of their boiling point.

An endeavour has also been made to produce alpha-furylethylene by splitting off water from the secondary α-furylethyl alcohol by heating it with $KHSO_4$, but it was found that the derived furylethylene polymerizes already during the distilling operation with the formation of a resinous body; the addition of anticatalytic agents that prevent the polymerization (e.g., hydroquinon), as it was recommended by Moureau,[143] was inadmissible in this case, since the presence even of traces of inhibition could afterwards affect the polymerizability of the furylethylene. It is evident, however, that furylethylene polymerizes more easily than styrene.

Table 5.—Physical Constants of Monomers.[142]

	Molecular Refraction	Molecular Refraction	Refractive							

Table 5.—Physical Constants of Monomers.[142]

Name	Constitution	Boiling point T °C.	Specific gravity at °C.	Refractive Index n_D	Molecular Refraction, found MK_D	Molecular Refraction, calculated MK_D
Styrol	$C_6H_5 . CH=CH_2$	33–34 (at 7 mm. Hg.)	0.8923 (24°)	1.5446 (24°)	36.81	35.07
o-Bromstyrol	$o-BrC_6H_4 . CH=CH_2$	102–104 (22 mm. Hg.)	1.409 (15°)	1.592 (15°)	43.96	42.84
p-Bromstyrol	$p-BrC_6H_4 . CH=CH_2$	102–104 (20 mm. Hg.)	1.408 (18°)	1.586 (18°)	43.61	42.84
Bromstyrol from brominated phenylethyl alcohol	$BrC_6H_4 . CH=CH_2$	98–100 (20 mm. Hg.)	1.403 (15°)	1.584 (15°)	43.66	42.84
o-Methoxystyrol	$o-CH_3OC_6H_4 . CH=CH_2$	85 (15 mm. Hg.)	1.009 (16°)	1.556 (16°)	42.74	41.22
p-Methoxystyrol	$p-CH_3OC_6H_4 . CH=CH_2$	104 (20 mm. Hg.)	1.0015 (17°)	1.560 (17°)	43.30	41.22
o-Aminostyrol	$o-H_2NC_6H_4 . CH=CH_2$	102–104 (12 mm. Hg.)	1.015 (15°)	1.608 (15°)	40.58	38.50
p-Aminostyrol	$p-H_2NC_6H_5 . CH=CH_2$	125–127 (10 mm. Hg.)	1.0216 (14°)	1.619 (14°)	40.91	38.50

Table 6.—Products of the Polymerization.[142]

Name of the monomer	Polymerization at 100°C.					Polymerization at 170°C.					Characteristics of the polymerizates
	$\eta_{sp.}$ at 20°C.	GM	M	P	T °C.	$\eta_{sp.}$ at 20°C.	GM	M	P	T °C.	
Styrol	0.1873	0.00961	108,218	1,040	95–97	0.0632	0.00961	36,515	351	90–92	Transparent, colourless resin, hard and resilient
o-Bromstyrol	0.1896	0.00546	96,395	526	105–110	0.1122	0.00546	57,029	311	95–100	Very hard transparent resin, resistant to ageing
p-Bromstyrol	0.06707	0.00546	34,099	183	—	0.04939	0.00546	25,106	137	—	Transparent, colourless resinous mass
Bromstyrol from brominated phenylethyl alcohol	0.17926	0.00546	91,123	497	—	0.10487	0.00546	53,308	291	—	—
o-Methoxystyrol	0.06707	0.00746	24,965	186	—	0.04883	0.00746	18,175	135	—	Brown-greenish resin-like mass
p-Methoxystyrol	0.10975	0.00746	40,851	304	—	0.09207	0.00746	34,270	255	—	
o-Aminostyrol	0.04104	0.00840	27,132	228	—	0.03275	0.00840	21,651	182	72–75	Brittle, yellow vitreous mass
p-Aminostyrol	0.02653	0.00840	20,005	168	78–80	0.03076	000.840	17,533	147	65–67	Brittle mass, with colour of colophony

Laboratory Procedure

The unsaturated compounds as characterized in Table 5 were polymerized at 100 degrees C., kept for 150 hours, and, in the parallel experiments, during three hours at 170 degrees C., employing in both cases the sealed glass tubes for performing the reactions, which were effected in absence of catalytic agents. The use of activators was purposely avoided in order not to complicate the polymerization processes by a possible breaking up, branching or cyclization of polymeric chains, which may be influenced by the presence of a foreign activating body; in a number of occasions, the other workers pointed out, for example, that in many cases suitable catalytic substances promote and accelerate the reaction, but the degree of polymerization thereby induced is of a lower order and the properties of products are different from those obtained by polymerizing in the absence of the catalysers.

Determination of the specific viscosity of diluted solutions (0.1 per cent. concentrations) of the derived products in toluol, and the estimation of the molecular weight and the degree of the polymerization have been made with the aid of Staudinger's equation: $\eta_{sp}=K_m.C.M$, where the symbols designate the same factors as described before. Since, however, the polymers formed are, undoubtedly, non-uniform in the sense that they make a mixture of one or another polymer-homologous series possessing various degrees of the polymerization, it follows that the viscosimetric method of Staudinger, in application to unfractionated (by the fractional precipitation or solubility) products, may give only an average molecular weight or, more precisely, a mean length of the molecules, where specific viscosity is strongly influenced, in the sense of augmenting its value, by the presence of molecules with relatively greater length.

In the case of polystyrenes the evaluation of the molecular weight is aggravated the more that macromolecules might have, apparently, not a strictly linear, but somewhat different shape, for instance, meandrine or spiral arrangements, as suggested by de Boer[144] on the basis of stereochemical considerations. Apart from this, there should be taken into account the possibility that during the polymerization of styrols a high branching or cyclization may take place, as frequently was pointed out in Staudinger's works. These possible deviations from linearity of polystyrol molecules provide an explanation for the divergence values of the molecular weights as determined for identical products by viscosimetric and osmometric means, where the latter method often gives much higher figures. It is also to be noted that the polymerization products of o- and p-aminostyrenes proved to be insoluble in toluol; for this reason their specific viscosity had to be determined by dissolving them in pyridine, in which they are easily soluble. Owing to non-availability of any indications either in Staudinger's works or elsewhere, in regard to constant K_m for the pyridine solutions of polystyrenes it was necessary to make the comparative evaluation of the specific viscosity of the identical specimens of polystyrols in pyridine and the toluol solutions (of the same concentration). This has revealed that the specific viscosities differ but slightly in both solvents. This is probably explained by the circumstance that, according to Staudinger's[145] data, in the case of solutions formed by homopolar high molecular compounds in homopolar solvents, the specific viscosity, in general, depends very little on the nature of solvent, provided it possesses a really strong dissolving power. On these grounds it has been considered permissible to accept, in the first approximation, for the pyridine solutions of polystyrols, the same constant $K_m = 1.8\times10^{-4}$, as for polystyrol solutions in toluol.

Table 6 summarizes the results obtained, giving also the information on the thermal stability and the physical characteristics of the polymerizates; in this Table η_{sp} stands for the specific viscosity of 0.1 per cent. toluol solution of polymers (in the case of aminostyrenes—of pyridine solutions of equal concentra-

tion), all other symbols denote the same factors as described in earlier part of this Section.

The rest of the monomers used (viz., octane-1, cyclohexylethylene, anethol, eugenol, iso-eugenol, symmetrical phenylmethylethylene, non-symmetric phenylmethylethylene, non-symmetric diphenylethylene, ω-bromstyrol, stilbene) undergo no change during polymerization, i.e., remain unpolymerized products; this has been checked by determining their molecular weights by the cryoscopic method in benzene solutions. Of all these substituted ethylenes some small tendency for the polymerization has been displayed only by cyclophexylethylene, yielding a product, whose molecular weight showed it to be a mixture of monomer and dimer. It should be recalled that Staudinger[146] has already succeeded in obtaining the polymer of cyclohexylethylene, but by a totally different method,—namely, by means of catalytic hydrogenation of hemicolloidal polystyrol in presence of nickel in decalin solution, forming thereby polymer-analogous polyhexahydrostyrenes.

Stilbene also was unaltered on heating, for its temperature of fusion remained the same (125 degrees C.), and as regards α-bromstyrol, it has been decomposed at the first attempt to polymerize it.

Discussion of Results

The study of the results of the above-described experiments enabled the authors to arrive at several conclusions with regard to the relationship between the polymerizability of substituted ethylenes (styrols) and their structure during the thermo-polymerization effected without the use of catalytic agents:—

A.—The prime pre-requisite is the presence of an aromatic nucleus directly substituting one of the hydrogen atoms of ethylene, i.e., the conjugation of the ethylenic double bond with the double bonds of the aromatic nucleus. If this conjugation is interfered with by the presence of even a single intermediate atom of carbon, the ability for the polymerization vanishes. On account of absence of aromatic nucleus, hexylethylene and cyclohexylethylene do not polymerize under the conditions stated, and, due to the absence of the conjugation, are not polymerizable saphrol and eugenol; only hexylethylene showed an embryonic tendency for the polymerization, but failed to form high molecular weight polymers.

The work of Gilman[147] demonstrated that furane possesses aromatic character, which is even more pronounced than benzene itself, and this is probably the reason of the extraordinary capacity of α-furylethylene for polymerization, owing to which it was possible to obtain monomer without adding anticatalysers.

B.—The polymerizability depends upon the degree of the molecular symmetry, which may be probably explained by consideration that, with the increasing degree of symmetry, generally, grows also the stability and often diminishes the reactionability of a substance; for instance, this is clearly manifested by the spontaneous regrouping of unsymmetric combinations into their isomeric compounds, as has been observed on numerous occasions; thus, the inability for polymerization, under the above conditions, was shown, for example, by the symmetric phenylmethylethylene, stilbene and anethol.

C.—The substitution of styrol in the α- as well as in β-position prevents polymerization, which has been observed in the cases of unsymmetric phenylmethylethylene, iso-safrol, and iso-eugenol. This phenomenon is probably due to the circumstance that these additional groups hinder steric orientation of side branches of polystyrene chains, as, for instance, in the event of meandrine or spiral schemes: the spatial arrangement of these supplementary branches must inevitably be at a certain distance from one another, when it may invalidate the electrostatic forces in their mutual repulsion.

D.—The capacity for polymerization diminishes with the increase of the molecular weight and the length of aromatic radical which substitutes hydrogen in the ethylene molecule. For example,

brominated styrol nuclei give products of the lower degree of polymerization than styrene itself, in consequence of almost duofold increase in weight of the nucleus; of isomeric bromstyrols p-bromstyrene polymerizes considerably worse than o-bromstyrene (due to lengthening of radicals).

The phenomena of a similar nature are observed in the cases of aminostyrols and methylstyrols. The sole exception from this regularity appears to be methoxylated styrenes; however, this exception is possibly only apparent, for it is necessary to take into account that estimation of the specific viscosity represents, strictly speaking, not molecular weight, but the average length of the molecules; the presence of methoxyl groups in one or another position can then exert a special influence on the molecular configuration of a polymer formed, affecting thereby also the molecular length (at the same degree of polymerization) as well as the specific viscosity of solutions.

E.—As frequently was pointed out also by other workers, for instance, by Staudinger, the progress of the polymerization reaction strongly depends upon the temperature used: the elevation of the temperature range accelerates the process in a very appreciable measure, but at the same time reduces the degree of the polymerization.

The aforesaid deductions made on the basis of extensive experimental studies find their support also in the scattered data of other authors, who conducted the researches on the polymerization processes, mostly in the presence of catalysts, and in some cases under great pressures.

For example, according to Staudinger and Dreher,[148] symmetric phenylmethylethylene or propenylbenzene, $C_6H_5.CH = CH.CH_3$, can be polymerized with great difficulty—even with the help of the most powerful catalysts (BF_3), it yields only products of low molecular weight (with molecular weight 1,000-3,000); aromatic allyl compounds, $Ar-CH_2-CH=CH_2$, are not polymerizable under those conditions, which favour the polymerization of corresponding propenyl combinations, etc.

Schmitz - Dumont, Thömke and Diebold,[149] who investigated the polymerization of a series of unsymmetric derivatives of diphenylethylene in ice acetic acid in presence of sulphuric acid, draw the attention to the dependence of the ability for polymerization on the non-symmetry of the molecules of substituted products of ethylene. These workers connect the polymerizability with the polarity of both carbon atoms united by the double bond, which depends on the degree of molecular symmetry; in their opinion, both the absence of polarity, as well as extremely strong polarity, prevent the polymerization.

(To be continued)

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